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THE MENTHOL GROUP.

BY LEO C. URBAN AND EDWARD KREMERS.

Two years ago, in a preliminary note to this Journal,[1] the discovery of a nitrosyl-chloride addition-product of menthene was announced. Since then we have published further work in connection with this subject, in the Proceedings of the American Pharmaceutical Association.[2] As these Proceedings have not a wide circulation among readers of this Journal, a short review of the work reported upon may serve as an introduction to this article.

The compounds which have been described are:

1. *Menthene*,[3] $C_{10}H_{18}$.—Prepared by the use of acid potassium sulphate as a dehydrating agent for menthol; boiling-point, 165° C. under pressure of 744 mm.; specific gravity at 20°, 0.8134; $[\alpha]_D = +31.83°$.

2. *Menthene nitrosochloride*,[4] $C_{10}H_{18}NOCl$.—Melting-point, 113°; $[\alpha]_D = +13.76°$. The melting-point (128°) of the nitrosochloride which was optically inactive, has since been observed.[4] v. Baeyer[5] has recently stated that the hydrocarbon obtained on dehydrating the tertiary menthol yielded a nitrosochloride melting at 146° "wie

[1] This Journal **14**, 232.

[2] Proc. Am. Pharm. Ass. 1892, 273; 1893, 185. [3] *Ibid.* 1892, 273.

[4] This nitrosochloride had been in contact with the mother-liquor for some time. When recrystallized from various solvents, as acetic ether, ether and chloroform, it showed in all cases the same melting-point (128°).

[5] Ber. d. chem. Ges. **26**, 2561.

gewöhnliches menthene." This apparent inconsistency may be explained by supposing the formation of stereometric isomers.[1]

3. *Menthene nitrosate*,[2] $C_{10}H_{18}N_2O_4$.—Melting-point, 98°; optically inactive.

4. *Menthene nitrosobenzylamine*,[3] $C_{10}H_{18}\left\{\begin{matrix}NO\\HNCH_2C_6H_5\end{matrix}\right.$.—Obtained either from the nitrosochloride or the nitrosate; melting-point, 107°; optically inactive.

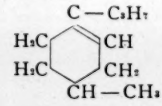
An attempt to prepare a piperidine base[4] proved unsuccessful. Piperidine evidently acts like the fixed alkalies on the nitrosochloride, splitting off hydrochloric acid with formation of nitrosomenthene. The study of the action of ammonia[4] upon the nitrosochloride has as yet yielded no definite results. Work in this line is now in progress.

5. *Nitrosomenthene*,[3] $C_{10}H_{17}NO$.—Obtained on treatment of the nitrosochloride or nitrosate with alcoholic potassa; melting-point, 67°; optically inactive.

An amido compound obtained upon reduction of nitrosomenthene by means of zinc-dust and acetic acid; its nitrate and its hydrochloride have been described under the name of menthylamine[4] and its salts. The results obtained upon analysis of the substances did not allow of a choice between the formulæ $C_{10}H_{19}NH_2$, a saturated cyclic compound, and $C_{10}H_{17}NH_2$, an unsaturated cyclic compound. This compound will be considered later.

For further details as to the above work the original articles are referred to. The following work in connection with this subject has been done since the publication of those articles.

Since v. Baeyer[5] has prepared the carvomenthene there can be but little doubt as to the position of the double bond in menthene. Assuming, then, the structure



for menthene, there are two possibilities as to the addition of nitrosyl chloride, namely :

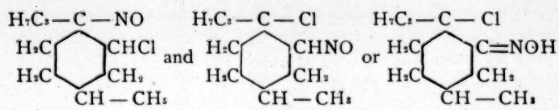
[1] The acid mother-liquor contains a large amount of nitrosochloride which cannot be separated in a solid form. (Ber. d. chem. Ges. **26**, 2561.)

[2] Proc. Amer. Pharm. Ass. 1893, p. 185.

[3] *Ibid.* 1892, p. 273; 1893, p. 185.

[4] *Ibid.* 1893, p. 185.

[5] Ber. d. chem. Ges. **26**, 824.



In order to ascertain the position in which the NO group is added in the nitrosochloride, an attempt was to be made to convert the so-called "menthylamine" into the corresponding alcohol through the diazo compound. If the NO group took the place of the hydroxyl group of the menthol, this compound should be regenerated from menthylamine; if it was added to the carbon atom next to the isopropyl group, a tertiary menthol was to be expected. The relative position of the groups has been established, but, as will be seen, in an entirely different manner from the one outlined.

Experimental Part.

The menthene employed was prepared according to Brühl's[1] method, using anhydrous copper sulphate as a dehydrating agent for menthol. Upon repeated fractionation with a column after Lebel and Henniger, a product was obtained boiling at 165.5° at a pressure of 739 mm.; specific gravity at 20°, 0.8132. In a 100-mm. tube it turned the plane of polarization 26.66° to the right: $[\alpha]_D = +32.77°$.

Nitrosochloride.—The nitrosochloride and, from it, the nitrosomenthene were prepared according to directions given in a former report.[2] The yield of nitrosochloride was slightly increased by frequent shaking of the mother-liquor after the separation of the first crop of crystals. From 780 cc. of menthene, 215 grams of the nitrosochloride were obtained, or about 4.11 grams from 15 cc., while the largest amount obtained without shaking the mother-liquor was below 4 grams from 15 cc. of menthene.[3]

The great stability of the nitrosochloride is shown in that it is apparently unaffected on boiling with water, dilute sulphuric acid and dilute potassa solution.

Nitrosomenthene.—When the nitrosochloride is heated by itself in quantities of a gram or more in a tube to about 115°, sudden decomposition takes place. Hydrochloric acid gas is given off and nitrosomenthene sublimes slowly, condensing in beautiful

[1] Ber. d. chem. Ges. **25**, 143. [2] Proc. Amer. Pharm. Ass. 1892, p. 273.
[3] *Ibid.* 1893, p. 185.

colorless needles in the upper part of the tube. A more rapid separation of the nitrosomenthene from the dark-colored by-products resulting in small quantity upon decomposition of the nitrosochloride in this manner, is effected by distilling the product with water-vapor. The nitrosomenthene passes over slowly, solidifying in the receiver to a white mass, which, when spread on a porous plate and dried, melts at 67° without further purification.

This method of purification has also been employed to separate it from the thick viscid mass remaining from the mother-liquor obtained upon recrystallization of the nitrosomenthene prepared by heating the nitrosochloride with alcoholic potassa.[1]

Reduction of nitrosomenthene.—Nitrosomenthene, melting at 66°–67°, was reduced by means of acetic acid and zinc-dust, and the resulting amido compound separated in the form of nitrate, as indicated in the previous work.[2] This base had been looked upon as a saturated compound, since from the method of reduction employed such a compound might be expected. Upon treatment with nitrous acid we had therefore anticipated the formation of a menthol $C_{10}H_{20}O$.

Alcohol, $C_{10}H_{18}O$.—20 grams of the nitrate were dissolved in acetic acid and 8 grams of sodium nitrite gradually added. An oily liquid separated slowly. When the reaction was completed the solution was made slightly alkaline and distilled with water-vapor. The oily liquid, which had a peppermint odor, was separated and exposed to cold. After some time small white crystals separated which melted at 89°–90° and were soluble in acidulated water. As this showed the presence still of basic matter, the oil was shaken with an aqueous solution of oxalic acid and again distilled with water-vapor. On attempting to fractionate the oil after drying, nitrous fumes were evolved. The heat was immediately removed and the substance heated for some time with a solution of potash to saponify any nitrous acid ester, and again driven over with water-vapor. The resulting product, separated and dried, yielded a main fraction passing over between 210°–215°; a little passed over below 210°, and some above 215°.

Fraction 210°–215° was analyzed with the following results:

I. 0.1298 gram gave 0.3705 gram CO_2 = 0.101045 gram C, and 0.1349 gram H_2O = 0.014988 gram H.

[1] Proc. Amer. Pharm. Ass. 1892, p. 273. [2] *Ibid.* 1893, p. 185.

II. 0.1779 gram gave 0.5078 gram CO_2 = 0.13849 gram C, and 0.1832 gram H_2O = 0.020355 gram H.

	Calculated for $C_{10}H_{20}O$.	Calculated for $C_{10}H_{18}O$.	Found. I.	Found. II.
C	76.92	77.91	77.84	77.84
H	12.82	11.68	11.54	11.44

Although the percentage of hydrogen is found rather low, the figures, as will be seen, correspond very well with those calculated for a compound $C_{10}H_{18}O$. An ethereal solution of the substance readily absorbed bromine, indicating that it is an unsaturated compound. When treated with chromic-acid mixture it formed a dark-colored chromic compound which liquefied upon raising the temperature. A secondary alcohol is thereby indicated. If the alcohol is an unsaturated compound, then the amido compound from which it is obtained must also be unsaturated; the formula $C_{10}H_{17}NH_2$ may therefore be assigned to it. All of these experiments are to be repeated, and a special study of the amido compound with regard to its saturation will be made.

Inactive menthone,[1] $C_{10}H_{18}O$.—In the preparation of the amido compound from nitrosomenthene there separated as a by-product an oily liquid having the odor of menthone. This was separated from the solution of zinc acetate and amidoacetate by distillation with water-vapor. The oily liquid was separated, dried and fractionated; fractions boiling between 204° and 206° and between 206° and 208° were obtained. Most of it passed over between 204° and 206°, and a small quantity remaining above 208°. Upon combustion fraction 204°–206° yielded the following results:

I. 0.2064 gram gave 0.5883 gram CO_2 = 0.160445 gram C, and 0.2198 gram H_2O = 0.024422 gram H.

II. 0.1690 gram gave 0.4781 gram CO_2 = 0.13039 gram C, and 0.1821 gram H_2O = 0.020233 gram H.

III. 0.1727 gram gave 0.4925 gram CO_2 = 0.134318 gram C, and 0.1850 gram H_2O = 0.020555 gram H.

	Calculated for $C_{10}H_{18}O$.	Found. I.	Found. II.	Found. III.
C	77.91	77.73	77.15	77.77
H	11.68	11.83	11.97	11.90

The figures found leave no doubt as to its composition. Its

[1] A notice of the isolation of this compound was given in a paper read before the Wisconsin Academy of Sciences, Arts and Letters, December 27, 1893.

boiling-point agrees very well with that of menthone. Its specific gravity at 18° C. was found to be 0.9071. It is optically inactive.

Like laevogyrate menthone it is readily converted into the oxime. It was heated for ten minutes in alcoholic solution with hydroxylamine hydrochloride and an excess of sodium bicarbonate in the proportions given by Beckmann[1] for the preparation of laevomenthoxime. The solution was filtered while hot and set aside to crystallize. Masses of needle-shaped crystals separated, which when spread on a porous plate and dried melted at 78°. The recrystallized product melted at 82°.

When hydrochloric acid gas is passed into a solution of the oxime in dry ether, a separation of the white crystalline hydrochloride takes place. An excess of the acid causes the precipitate to redissolve.

The ketone-character of the compound $C_{10}H_{18}O$ cannot be doubted. Beckmann and Pleissner[2] have obtained a menthone yielding an oxime melting at 84°–85°, from pulegone, a body having the composition $C_{10}H_{16}O$. This menthone they obtained by treating the hydrobromic acid addition-product of pulegone with zinc-dust. It was laevorotatory, whereas pulegone is dextrorotatory. The menthone regenerated from the oxime and again treated with hydroxylamine, they found to yield an oxime melting several degrees lower, *i. e.* at 78°–82°. It is therefore very probable that the menthone obtained as a by-product in the reduction of nitrosomenthene is the optically inactive modification of that obtained by Beckmann and Pleissner.

Menthol.—Fraction 204°-206° of the menthone was treated according to Beckmann's method[3] for the reduction of ketones. An ethereal solution was heated for some time with metallic sodium, the solution was then poured off from the excess of sodium and shaken with water. It was then removed from the water, the ether allowed to evaporate, the product again dried, dissolved in dry ether and treated a second time with metallic sodium. The resulting product was distilled with water-vapor and the oily liquid after separation exposed to cold. After some time it congealed to a crystalline mass. The crystals dried on a porous plate melted at from 24° to 26°. They were exposed to air for some time and then placed over sulphuric acid, but the melting-

[1] Ann. Chem. (Liebig) **250**, 329. [2] *Ibid.* **262**, 25.
[3] *Ibid.* **262**, 25; Ber. d. chem. Ges. **22**, 912.

point could not be brought above 29°–31°. The quantity obtained was too small to admit of purification by recrystallization or other means. The crystals had the pungent and cooling taste and odor of menthol, which is quite different from that of menthone. Larger quantities will be prepared and its properties more accurately determined.

The formation of menthol from menthone according to this process is represented by the following equations:

$$2C_{10}H_{18}O + Na_2 = C_{10}H_{17}ONa + C_{10}H_{19}ONa.$$
$$C_{10}H_{17}ONa + C_{10}H_{19}ONa + 2H_2O = C_{10}H_{18}O + C_{10}H_{19}OH + 2NaOH.$$
$$C_{10}H_{18}O + C_{10}H_{19}OH + Na_2 = 2C_{10}H_{19}ONa.$$
$$2C_{10}H_{19}ONa + 2H_2O = 2C_{10}H_{19}OH + 2NaOH.$$

The formation of menthone, $C_{10}H_{18}O$, a ketone, as a by-product in the reduction of nitrosomenthene in acid solution, indicated that nitrosomenthene is an oxime; that a partial hydrolysis of this oxime took place, hydroxylamine being split off, and the ketone $C_{10}H_{16}O$, which was probably formed, reduced by the nascent hydrogen to the saturated ketone $C_{10}H_{18}O$. It was therefore expected that the ketone $C_{10}H_{16}O$ could be isolated and nitrosomenthene regenerated on treating it with hydroxylamine.

Nitrosomenthene is comparatively stable towards sulphuric and acetic acids, but when warmed with hydrochloric acid, hydroxylamine is split off with great readiness.

Ketone $C_{10}H_{16}O$ *from nitrosomenthene.*—18 grams of nitrosomenthene were dissolved with the aid of a gentle heat in twice its weight of hydrochloric acid (sp. gr. 1.20), and diluted with an equal volume of water. The solution was warmed for a short time on a water-bath and then distilled with water-vapor. A colorless oil was carried over which became yellowish on exposure for a short time. It had a mild peppermint odor, reminding one somewhat of pulegone. It was dried with caustic potash and fractionated. Nearly all passed over between 210° and 212°, a small amount between 208° and 210°, and some above 212°. The acid liquid remaining in the flask on distillation of the hydrochloric-acid solution immediately reduced Fehling's solution, showing the presence of hydroxylamine.

Fraction 210°–212° had a specific gravity of 0.9150 at 20° and is optically inactive. The following results were obtained upon analysis:

I. 0.1676 gram gave 0.4818 gram CO_2 = 0.13140 gram C, and 0.1603 gram H_2O = 0.017811 gram H.

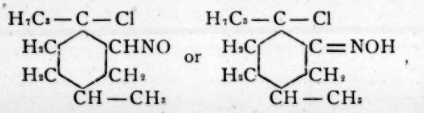
II. 0.2072 gram gave 0.5967 gram CO_2 = 0.162736 gram C, and 0.1994 gram H_2O = 0.0227 gram H.

	Calculated for $C_{10}H_{14}O$.	Found. I.	Found. II.
C	78.94	78.40	78.54
H	10.52	10.62	10.95

Oximido derivative, $C_{10}H_{16}NOH$.—To convert it into its oximido derivative, 3 grams of the ketone were dissolved in two and a half times its weight of alcohol and heated together with 2 grams hydroxylamine hydrochloride and an excess of sodium bicarbonate, for two hours on a water-bath, in a flask connected with a reflux condenser. The solution was filtered while hot and set aside. After the evaporation of the alcohol a thick viscid mass remained which was purified by distillation with water-vapor. The oxime congealed to a white crystalline mass in the receiver. When spread on a porous plate and dried it melted at 67°. Crystallized from methyl alcohol it was obtained in crystals having the characteristic form of nitrosomenthene and melting at 67°. The identity of the oxime with nitrosomenthene cannot therefore be doubted, and the presence of the oximido group in nitrosomenthene must be assumed.

Conclusions.

It will be seen from the above experiments that the nitrosyl-chloride addition-product of menthene has the structure

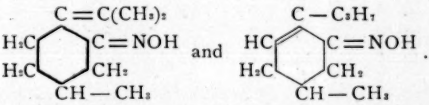


the formation of the ketone, $C_{10}H_{14}O$, of menthone, $C_{10}H_{18}O$, and of menthol, $C_{10}H_{20}O$, the corresponding secondary alcohol, leaving no doubt as to the position of the nitroso group or the oximido group, and consequently as to that of chlorine. According to Markownikow,[1] when an unsaturated body combines with a compound YZ at a comparatively low temperature, the more negative part will add itself to the carbon atom connected with

[1] Beilstein (3te Aufl.) Bd. I, 94.

the least number of hydrogen atoms, or that carbon which is already connected with a negative element or group. Nitrosyl chloride would seem, then, to follow this rule.

There are two possibilities as to the splitting off of hydrochloric acid from the nitrosochloride in the formation of nitrosomenthene: the chlorine going out with hydrogen so as to form a double bond connecting the side chain, or a double bond in the nucleus, as



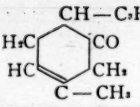
The latter, however, must be considered as the correct formula, the tendency being always towards splitting off with hydrogen in the nucleus. v. Baeyer,[1] in his experiments with menthene and carvomenthene, finds that on splitting off hydriodic acid from the tertiary iodides, menthene and carvomenthene are regenerated, and that it therefore seems impossible in this manner to obtain a tetrahydrocymene in which the double bond is partially or wholly in the side chain. The formation of nitrosomenthene from the nitrosochloride is entirely analogous. Semmler[2] has shown that in pulegone the double bond must be assumed as being in connection with the side chain; consequently if the first formula were assumed for nitrosomenthene, the ketone obtained from it should be identical with pulegone; but this is not the case.

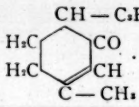
The oximido group in the nitrosomenthene has been shown. Whether the rearrangement of the nitroso group with the hydrogen into the oximido group already takes place in the nitrosochloride is still an open question.

Adopting the nomenclature of Wallach,[3] there are possible four β-ketones of the formula $C_{10}H_{16}O$ having the double bond in the nucleus, namely,

[1] Ber. d. chem. Ges. **26**, 2269. [2] *Ibid.* **25**, 3515.

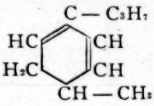
[3] Ann. Chem. (Liebig) **277**, 105. Wallach distinguishes between α- and β-ketones of the hydrocymenes: the α-ketones are those in which the carbonyl group is in the ortho position with the carbon atom connected with the methyl group, while β-ketones are those in which it is nearest to the isopropyl group.





The ketone from nitrosomenthene is the first of these, and so far the only one known. Pulegone, a constituent of the oils of *Mentha pulegium*[1] and of *Hedeoma pulegiodes*[2] is also a β-ketone of the formula $C_{10}H_{16}O$, but has the double bond connected with the side chain.

The alcohol $C_{10}H_{18}O$ from the amido compound $C_{10}H_{17}NH_2$ must be the same as that to be expected upon reduction of the ketone $C_{10}H_{16}O$. Upon dehydration this may be expected to yield a terpene



which would be the first body of this class the structure of which could be definitely stated.[3]

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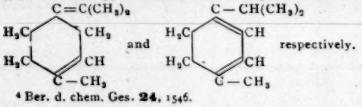
KETONES FROM PINENE DERIVATIVES.

BY LEO C. URBAN AND EDWARD KREMERS.

Wallach[4] states that nitrosopinene is not affected by acids; that even when warmed with concentrated sulphuric acid it is again separated unchanged upon diluting with water. This, he says, can only be explained by assuming that in isomeric nitroso

[1] Ann. Chem. (Liebig) **262**, 25. [2] Proc. Wis. Pharm. Assoc. 1893, 51.

[3] Since writing this manuscript a paper by v. Baeyer has appeared (Ber. d. chem. Ges. **27**, 442) in which it appears that formulæ of terpinolene and of dipentene must be considered as



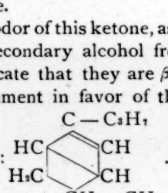
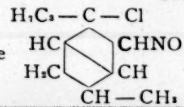
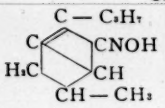
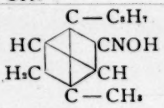
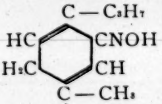
respectively.

[4] Ber. d. chem. Ges. **24**, 1546.

compounds the group =NOH is contained, whereas in nitrosopinene the group —N=O is present.

Nitrosomenthene, which undoubtedly contains the oximido group, is also very stable towards sulphuric acid, but when warmed with hydrochloric acid is easily decomposed with formation of a ketone. When nitrosopinene is treated in like manner with hydrochloric acid it readily decomposes into an oily body, probably a ketone, $C_{10}H_{14}O$, and hydroxylamine, the presence of which is readily shown in the acid liquid by its reducing power on Fehling's solution. This body is now undergoing investigation.

Wallach has observed a ketone $C_{10}H_{16}O$ among the decomposition-products of pinylamine hydrochloride when heated, and which he admits[1] may come from an impurity in the salt. This body may possibly owe its origin to a reaction during the reduction of the nitrosopinene with zinc and acetic acid, similar to that taking place upon reduction of nitrosomenthene causing the formation of menthone.

The peppermint odor of this ketone, as well as that obtained upon oxidation of the secondary alcohol from pinylamine, $C_{10}H_{14}O$,[2] would seem to indicate that they are β-ketones, and may be considered as an argument in favor of the first formula set up by Wallach for pinene:  . The nitrosochloride then would be  , and the nitrosopinene  or  , which may possibly rearrange itself into  . The peppermint odor of

[1] Ann. Chem. (Liebig) **268**, 210. [2] Wallach: Ann. Chem. (Liebig) **277**, 150.

the ketones obtained by Wallach would appear to speak for some such rearrangement of the bonds in these ketones, since, if the para bond or bonds remained intact, the bodies might be expected to have a camphoraceous odor.

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RESEARCHES UPON THE PHENOMENA OF OXIDATION AND CHEMICAL PROPERTIES OF GASES.

BY FRANCIS C. PHILLIPS.

[*Concluded from page* 365.]

V.—COMPOSITION OF NATURAL GAS.

The gas used in the following trials was that supplied to Allegheny by the Allegheny Heating Company, and is the product of wells scattered over a considerable gas-producing area. It may be said to represent the average composition of an enormous volume of gas. No important differences have been observed during the period from 1886 to 1892 in the heating or illuminating power of the gas as supplied to the city, although the odor of petroleum (*i. e.* of higher paraffins) has been occasionally stronger.

Tests have also been made of gas from various localities in Pennsylvania, New York and Indiana, and Vancouver, British Columbia, and also at Cleveland, Ohio. In all cases where possible the tests were made at the wells. When this could not be done it was necessary to use samples brought in glass vessels to the laboratory. In such cases the samples were examined for oxygen before being subjected to the tests. As a leak in a sample-vessel invariably causes an interchange of air and gas, so that air enters in proportion as an escape of gas occurs, much dependence is to be placed on the presence or absence of air in a gas-sample as a criterion of its purity.

Hydrogen.—Hydrogen is almost always mentioned in the published analyses of natural gas. I have made the following

chemical tests: The natural gas, as supplied to Allegheny by the Allegheny Heating Company, was caused to flow through a solution of palladium chloride for periods varying from ten days to three months; 500 cubic feet have been used in a single experiment. Similar tests have been repeated at various times between January, 1886, and May, 1892, but in no case was a trace of precipitation observed in the palladium-chloride solution. Natural gas was found likewise to be without action upon solutions of platinum chloride and ammoniacal silver nitrate. A stream of natural gas has been passed through pure *dry* palladium chloride. This extremely delicate test has failed to show the presence of hydrogen even in traces, although tried repeatedly during the period from January, 1886, until May, 1892. As already stated, the results of my study of gas-reactions show that palladium chloride produces very different effects according as it is used dry or in solution. Palladium chloride *dry* is reduced promptly by dry hydrogen when the gas is used in a free state.

The same salt in solution is slowly and incompletely reduced by hydrogen, although it is rapidly reduced by olefines and carbon monoxide. Similar tests with palladium chloride, both dry and in solution, made at the wells, in the cases of all the localities mentioned in the table No. I, from 1 to 14, have led to similar results. Natural gas from Vancouver and from Kokomo, Indiana, could not be tested at the wells. Tests made in the laboratory, of the samples received from those localities, gave the same negative results.

Another method of testing for hydrogen has been employed: As is well known, a jet of hydrogen is immediately ignited by platinum asbestos. Natural gas under similar conditions is not ignited, even when the gas-jet and the platinum sponge are mounted in an oven kept at a temperature approaching 300°. In order to ascertain the effects of different proportions of hydrogen and natural gas, a gasometer containing the gas-mixture to be tried was connected with a tip in the form of a drawn-out glass tube, above which some platinum asbestos was fixed. The gas pressure could be so regulated as to produce a pointed flame one inch long. By momentarily shutting off the gas by pinching the hose the flame could be extinguished, and the gas, being turned on again, played against the platinum asbestos. The length of the flame when the gas stream from the jet was ignited was there-

fore a measure of the gas flow. The gas was ignited by the platinum asbestos or not, according as the proportion of hydrogen in the natural gas was greater or less. The ignition of the gas was also dependent upon the temperature of the oven in which the jet and the platinum asbestos were fixed.

Mixtures of hydrogen and natural gas produced glowing of the platinum and ignition of the gas at the following temperatures, when the experiment was made in a large iron oven whose temperature could be readily measured. The gas pressure was the same in all trials.

Proportion of Hydrogen and Natural Gas.	Temperatures of the Oven at which the Gas inflames as it strikes the Platinum Asbestos.
Natural gas .....95 Hydrogen..... 5	40°–50°
Natural gas .....97.5 Hydrogen..... 2.5	80°–90°
Natural gas.....99 Hydrogen..... 1	180°
Natural gas .....99.5 Hydrogen..... 0.5	210°–220°
Natural gas .....99.75 Hydrogen..... 0.25	270°
Pure natural gas.....	270°–290°

The observed temperatures naturally vary with the pressure, size of jet, etc., but trials with different pressures showed greater constancy than could be anticipated from a method so rough in appearance. The results corroborate those obtained by the more delicate tests. Experiments have also been tried with mixtures of air and natural gas which were exposed to palladium asbestos contained in glass tubes heated in the iron oven described under "Oxidation-temperatures of Hydrocarbons." It has been repeatedly shown that, under such conditions, moisture is produced only at temperatures approaching or higher than the melting-point of cadmium iodide.

The absence of free hydrogen has interfered with the use of natural gas in gas engines. The prompt, sharp explosion of coal-gas, so necessary for these motors, cannot be produced in the case of natural gas, which requires a higher temperature for its ignition, and explodes with less suddenness owing to the absence of hydrogen.

The electrical devices for the igniting of coal-gas jets in dwellings by the spark of an induction-coil have not been so successful

where natural gas is used, owing to the higher temperature of ignition of a gas consisting of paraffins and containing no hydrogen. In laboratories where natural gas is the fuel, chemists have experienced the inconvenience that Bunsen burners and blast-lamps do not produce the high temperature easily obtained when coal-gas is used. Ordinary glass combustion-tubing cannot be softened by the employment of natural gas in a Berzelius blast-lamp.

A coal-gas flame owes it steadiness and "stiffness" to the hydrogen which the gas contains. Natural-gas flames are much less steady and more easily extinguished by air currents.

During May, 1892, a change occurred in the composition of the natural gas supplied to Allegheny City. The gas since that time and up to November, 1892, has been found to contain hydrocarbons which reduce *dry* palladium chloride. These hydrocarbons are removed completely by digestion with fuming sulphuric acid, so that the gas after this treatment does not reduce palladium chloride. The nature of these hydrocarbons I have been unable yet to determine.

Olefines.—Palladium chloride, iridium chloride, cerium dioxide in sulphuric acid, osmic acid, all remain unchanged by natural gas, cold or at 100°. Potassium permanganate is attacked with extreme slowness.

Bromine-water has been repeatedly tried. The solution was in some cases cooled by ice to check evaporation of the bromine, and in others the bromine was added slowly, drop by drop, to compensate for its evaporation. In no case were any oily drops produced. Prof. Sadtler, of Philadelphia, has in one instance obtained a considerable amount of heavy oil by the action of bromine on natural gas.

My experiments seem to prove the absence of ethylene, propylene, isobutylene and trimethylene from the gas supplied to Allegheny. The same is true of gas from the localities mentioned in the table from 1 to 17. Tests could not be made at the wells in the case of gas from Kokomo, Indiana, and Vancouver, British Columbia, but samples brought to the laboratory gave similar results.

The very low illuminating power of the natural gas of Western Pennsylvania is a further evidence of the absence of olefines, which, as is well known, are remarkable for the brilliancy of the light which they produce. By the kindness of Mr. J. W. Patterson, gas

inspector of Allegheny county, I am able to give the following data as to illuminating power: The gas supplied to Pittsburgh by the mains of the Philadelphia Company, November 30, 1892, possessed an illuminating power equal to $10\frac{84}{100}$ candles per five cubic feet of gas burnt per hour (mean of ten determinations). On the same date the illuminating power of the natural gas supplied by the People's Natural Gas and Pipeage Company was $10\frac{77}{100}$ candles. Mr. Patterson's tests were made with a 36-hole Argand burner, having a chimney 7 inches long.

Acetylene and Allylene.—Palladium-chloride solution is unchanged, as already stated. Cerium dioxide, mercuric chloride, gold chloride, silver nitrate, ammoniacal cuprous chloride and osmic acid are all unchanged. Hence, in the gas I have tested it may be said that no hydrocarbons of the acetylene series occurred.

I have found no reference to acetylenes in any published analyses to which I have had access.

Carbon Monoxide.—In the published analyses of natural gas, carbon monoxide is nearly always stated to occur. In my experiments, palladium chloride, gold chloride, silver nitrate in ammonia, iridium chloride, rhodium chloride, osmic acid, all used in solution, were unchanged.

Experiments have been made with Allegheny City natural gas in the following way: Gas has been caused to bubble for five weeks through ammoniacal cuprous-chloride solution. This solution was then largely diluted with water and boiled. The gases expelled were collected and tested by palladium-chloride solution, but no carbon monoxide was found. It is true that, since the absorption of carbon monoxide in cuprous chloride has been shown to be a case of mechanical solution rather than chemical union, and that the absorbed monoxide can be expelled by a stream of other gases, the use of cuprous chloride for the absorption and recognition of carbon monoxide cannot be implicitly depended on. Still, the direct tests above named lead me to the conclusion that no carbon monoxide occurs in our natural gas.

Paraffins.—That the lower paraffins occur in natural gas needs no proof. Methane is the chief constituent. Small quantities of higher paraffins are usually present.

Sulphur Compounds.—Pennsylvania natural gas does not contain recognizable quantities of either carbon oxysulphide, methyl hydrosulphide or methyl sulphide. Towards the western boun-

dary of the State it is possible that minute traces of sulphuretted hydrogen occur. The quantities of all such compounds are far too small to allow of their being easily identified, even in the case of large volumes of gas. The extreme delicacy of the reaction of methyl mercaptan towards palladium chloride would render it possible to detect exceedingly minute quantities of this compound should it occur.

I have not had an opportunity to test the gas from the Western Ohio territory, which is said to contain sulphur compounds in considerable quantity.

Nitrogen.—Natural gas, dried by calcium chloride and phosphorus pentoxide, was passed over strongly heated magnesium powder. The magnesium was partly converted into a nitride, easily recognized by its reaction towards moisture, yielding ammonia in considerable amount.

Repeated trials have been made of natural gas in the following way: A measured volume of gas was passed over ignited oxide of copper contained in a porcelain tube, the entire apparatus having been previously filled with pure carbon dioxide, which was caused to flow in a continuous stream for several hours in order to expel all traces of air. The escaping gas was collected in a eudiometer over mercury and the carbon dioxide absorbed by soda. There was left invariably a residue of gas unabsorbed by the soda and having no action upon palladium-chloride solution. This residual gas was evidently nitrogen.[1] In the gas found in an artesian boring at Middlesborough, England, nitrogen was found in large proportion.[1]

Oxygen.—By the use of pyrogallol and soda, and by the oxidation of manganous hydrate in water, I have frequently been able to detect traces of oxygen, although on other occasions no oxygen could be found. It has only been recognized when the gas had bubbled continuously for many hours or days through the reagent. It cannot be said that oxygen is a constant constituent, although it does unquestionably occur in much of natural gas in minute traces.

Carbon Dioxide is present in all natural gas, as is easily proved by its action upon lime-water.

Ammonia.—In the case of a gas-well near Canonsburg, the following result was obtained: Gas was caused to bubble directly

[1] See Table of Analyses, p. 422.

from the main at the well through water for several hours. On applying Nessler's reagent to the water, a feeble reaction was obtained. Ammonia was not found elsewhere in the trials I have made. Mr. S. A. Ford, of the Edgar-Thompson Steel Works, reports a very interesting case where masses of solid ammonium carbonate were blown out from a gas-well by the pressure of the gas.

Natural gas appears to consist chiefly of methane, with traces of higher hydrocarbons of the paraffin series. Nitrogen is probably always present, together with a little carbon dioxide. The absence of free hydrogen, of olefines and of carbon monoxide is, I believe, clearly shown in the case of the natural gas I have examined.

If natural gas as found in the wells of any one gas-region is derived from one vast subterranean reservoir, approximate uniformity in composition should be looked for. It is often noticed, however, that gas from adjacent wells possesses a different odor. A carbon-dioxide determination was made in the case of samples of gas from six wells near Tarentum, Pa. These wells were situated nearly on a straight line less than one mile in length. The samples were all taken within an interval of three hours. The determinations were made with a 7-per cent. soda solution in a eudiometer over mercury.

Well.	Carbon Dioxide.	Well.	Carbon Dioxide.
No. 1,	0.42 per cent.	No. 4,	1.47 per cent.
2,	1.25	5,	1.28
3,	0.25	6,	1.28

The differences in the proportion of carbon dioxide—a constituent determinable with great precision—would be difficult to explain if the gas flowing from these different wells is derived from one subterranean reservoir.

VI.—Quantitative Analysis of Natural Gas.

It is not possible to determine the proportion of the individual paraffins in a gas-mixture by the Bunsen method of explosion with oxygen unless it can be positively asserted that only two paraffins occur. This may be readily shown by an example. If a mixture of one volume each of marsh-gas, ethane and propane is burnt, the volumes of oxygen required, carbon dioxide and steam produced will be as follows:

	Oxygen Required.	CO_2.	H_2O Vapor.
1 vol. methane,	2 vols.	1 vol.	2 vols.
1 " ethane,	3½	2	3
1 " propane,	5	3	4
	10½	6	9

Three volumes of ethane require for combustion ten and one-half volumes of oxygen, and yield six volumes carbon dioxide and nine volumes of steam. Hence a mixture of three gaseous paraffins could not be distinguished, in the case of a volumetric analysis, from the intermediate paraffin. Moreover, the heat of combustion of three volumes of the intermediate paraffin is almost exactly equal to that of a mixture of one volume each of the three. From this fact it follows that, as regards the calorific value of a mixture of paraffins, an exact determination of the character of the individual paraffins is not required.

A saving of time, the possibility of using a larger volume of gas, the avoidance of a volumetric determination of water-vapor, are some of the advantages gained by a combustion over copper oxide.

The application of gravimetric methods for the examination of gas is not new. Winkler[1] has described such a process for the analysis of mine-gas.

Description of Method.—The process employed was, with some slight modifications, the same as described in the Annual Report of the Geological Survey of Pennsylvania for 1886: Glass cylinders having stop-cocks at both ends, accurately calibrated by mercury and of 300–400 cc. capacity, were filled with natural gas. Where possible, this was done at the well. Before filling with gas, finely drawn-out threads of glacial phosphoric acid were inserted through the stop-cock into the vessel.[2] After twenty-four hours the gas sample could be considered dry. The cylinder was then connected with a porcelain combustion-tube, *C*, containing copper oxide. The general arrangement of the apparatus is shown in the accompanying sketch.

Before the communication was made between the tube *C* and the glass cylinder *A*, air was expelled from *C* by pure nitrogen

[1] Handbook of Technical Gas Analysis, p. 87.

[2] Glacial phosphoric acid, on softening in the flame, may be readily drawn out like glass into rods of almost hair-like fineness. The quantity required was not sufficient to cause error in the gas measurements, inasmuch as the gas as it flows from the wells is in most instances remarkably dry.

dried in the tubes *M*. The combustion-tube was intensely heated during the passage of the nitrogen. After expulsion of air by nitrogen, the natural gas was caused to flow over the copper oxide previouly heated for some time. The movement of the gas through the combustion-tube was controlled by means of mercury, which flowed from the funnel *D* into the gas-cylinder, and was so regulated that two hours were required for complete combustion. Experiments showed that there is no danger of production of carbon monoxide or unsaturated hydrocarbons when the gas-stream is slow. After the gas had been expelled from the cylinder *A*, it was rinsed by lowering the mercury funnel so that nitrogen passed down into the cylinder, to be again driven out by raising the funnel.

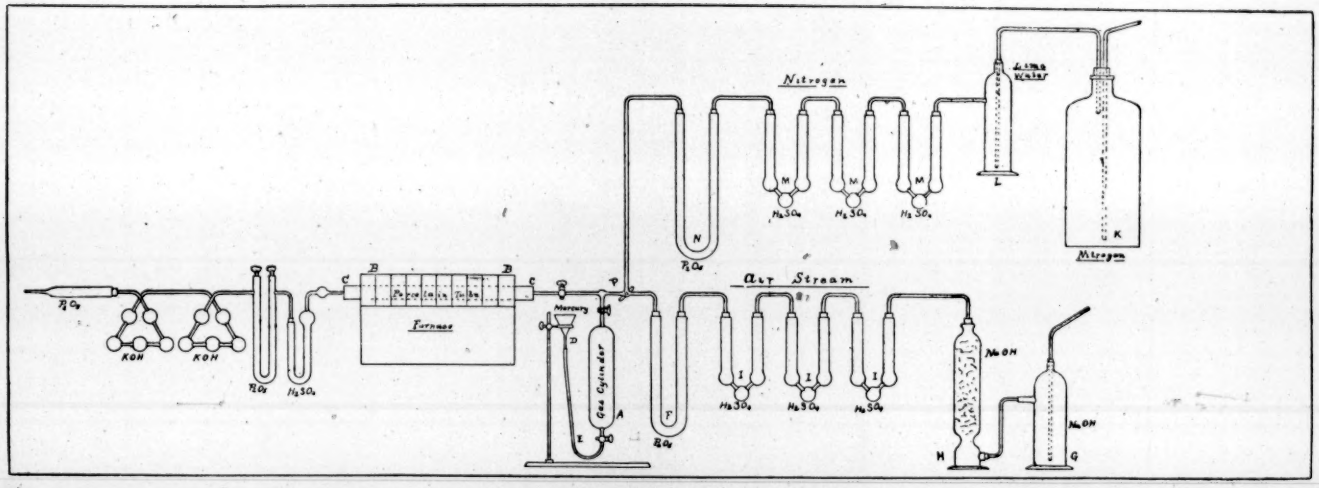
After the gas had been fully burned, air (purified by the lower system of drying-tubes in the sketch) was passed through the apparatus till the nitrogen and moisture had been fully displaced and the process was then complete, the carbon dioxide and water being determined by weight. The method, as is seen, gives merely the proportions of carbon and hydrogen. As the exact percentage of the paraffins in the gas-mixture cannot be ascertained by analysis, an approximation alone is possible.

The composition by weight of some of the lower (gaseous) paraffins is as follows:

Paraffins.	Carbon.	Hydrogen.
Methane,	74.97 per cent.	25.03 per cent.
Ethane,	79.96	20.04
Propane,	81.78	18.22
Butane,	82.72	17.28

In the following table, the calculated composition by weight of various mixtures of methane and ethane is given (the atomic weight of carbon being 11.97):

Mixture of Methane.	Ethane	Carbon.	Hydrogen.
1 vol.	1 vol.	78.22 per cent.	21.78 per cent.
3	2	77.73	22.27
2	1	77.38	22.62
5	2	77.11	22.89
3	1	76.89	23.11
7	2	76.70	23.30
4	1	76.56	23.44
5	1	76.30	23.70
6	1	76.15	23.86
9	1	75.82	24.18



Apparatus for Quantitative Analysis of Natural Gas.

From a gravimetric analysis of natural gas it is easy to determine the relative proportions by weight of carbon and hydrogen in unit volume, and from these the composition may be stated volumetrically in terms of ethane and methane, by the use of the preceding table, and with a fair approximation to the truth. It is probable that minute quantities of propane and perhaps higher paraffins occur, but these cannot be identified. The nitrogen and carbon dioxide being determined, the volume of

$$CH_4 + C_2H_6 + C_3H_8 + \ldots\ldots$$

is obtained as a difference. The error involved in such a method may then be exactly defined as follows: The hydrocarbons may consist of methane with traces of propane, or of methane with ethane or butane, but the analysis will be stated volumetrically in terms of methane and ethane only.

As regards the question of fuel value, I have endeavored to show[1] that the above method will give closely approximate results when certain factors relating to available heat of combustion of paraffins are used. The gravimetric method affords at the same time a means of control, for it is not only true that in a given volume of a particular paraffin, or of a mixture of paraffins, the hydrogen and carbon will occur in definite quantity, but the ratio $\frac{C}{H}$ is a constant, and will be greater as the proportion of higher to lower paraffins is greater. These considerations will serve to show the limits of accuracy of the method.

Nitrogen was determined by passing a measured volume (100 cc.) over ignited copper oxide contained in a porcelain tube, and then into a eudiometer containing soda solution. By means of a stream of carbon dioxide continued for several hours, the air was expelled from the apparatus previous to the combustion of the gas. In presence of a large excess of carbon dioxide, combustion by copper oxide is greatly retarded, and the process must be conducted very slowly to effect complete oxidation.

Oxygen, as already stated, occurred in too small proportion to allow of a quantitative determination.

Carbon dioxide was determined by soda solution in a eudiometer over a mercury trough.

[1] See Rep. Geol. Surv. Penna. 1886.

ANALYSES OF NATURAL GAS.

CONSTITUENTS.	Fredonia, N. Y. 1	Sheffield, Warren Co., Pa. 2	Kane, McKean Co., Pa. 3	Wilcox, McKean Co., Pa. 4	Speechly, near Oil City, Pa. 5	Lyons Run, Murrysville, Pa. 6	Raccoon Creek, Pa. 7	Houston, near Canonsburg, Pa. 8	Murrysville, Pa. 9	Pittsburgh Exhibition Grounds, Pa. 10	Cleveland, O. 11	Creighton, Pa. 12	Painter & Co.'s Well, Pittsburgh, Pa. 13	Baden, Pa. 14	Kokomo, Ind. 15	Allegheny City Salt Well. 16	Vancouver, British Columbia. 17
Nitrogen	9.54	9.06	9.79	9.41	4.51	2.02	9.91	15.30	4.40	7.30	6.30	0	0.70	12.32	6.00	7.10	6.30
Carbon dioxide	0.41	0.30	0.20	0.21	0.05	0.28	trace	0.44	0.20	0.52	0.20	3.64	0.40	0.41	0.40	0.30	0.14
Hydrogen	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ammonia	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Oxygen	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	0	0	0	0	0	0	0
Sulphuretted hydrogen	0	0	0	0	0	0	trace	0	0	0	0	0	0	0	0	0	0
Paraffins	90.05	90.64	90.01	90.38	95.44	97.70	90.09	84.26	95.40	92.18	93.50	96.36	98.90	87.27	93.60	92.60	93.56
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
The paraffins contained in these gas-samples have the following composition by weight:																	
Carbon	78.14	76.69	76.77	76.52	77.11	74.96	76.42	76.68	75.15	75.40	76.40	75.80	75.51	76.48	75.40	75.44	75.23
Hydrogen	21.86	23.31	23.23	23.48	22.89	25.04	23.58	23.32	24.85	24.60	23.60	24.20	24.49	23.52	24.60	24.56	24.77

Nos. 1, 2, 3, 4, 5, 6, 7, 8, 14 are cited from *Report of Geol. Survey of Penna.*, 1886.

Tests were made at the wells in all cases excepting Kokomo and Vancouver. In the case of these two localities samples were very carefully taken and forwarded by Mr. E. C. Somers (Kokomo) and Mr. C. F. Hutchings (Vancouver). (All the analyses were made by F. C. P.)

VII.—Origin of Natural Gas and Petroleum.

Soon after the early discoveries of oil and gas in Pennsylvania, geologists proposed an hypothesis to account for the origin of these remarkable substances: Remains of the marine vegetation of the Devonian inland sea, as they were gradually buried under the later accumulations of sediment and exposed to gentle heat from below, underwent a slow process of destructive distillation. In this way all the varieties of petroleum and natural gas were produced. This view, adopted from a purely geological standpoint, seemed so plausible that for a long period no other was thought of. Mr. J. F. Carll, of the Second Geological Survey of Pennsylvania, has discussed the hypothesis very exhaustively in his various official reports. If this view is correct, oil and gas are probably *stored products*, and are not being continuously generated at the present time.

Opposed to this view is the more strictly chemical hypothesis of Mendeléeff, who, in 1876, expressed his belief that petroleum and gas are of igneous origin. On account of the high value assigned by astronomers for the mean density of the earth as compared with that of the surface rocks, it follows that the heavy metals are mainly accumulated at great depths where a temperature of fusion may be assumed. Many of these metals combine readily with carbon to form carbides. Iron, in form of a carbide, when exposed to steam at high temperatures, is rapidly oxidized, the hydrogen of the water then combining with the carbon set free and producing hydrocarbons.

Citing experiments of Cloez, who produced mixtures of hydrocarbon oils by the action of hydrochloric acid upon ferromanganese, Mendeléeff concluded that such reactions have occurred at great depths below the earth's surface by the contact of steam with incandescent metallic carbides. "During the upheaval of mountain ranges, crevices would be formed at the peaks with openings upward, and at the foot of the mountains with openings downward. Thus there was opportunity for the water to penetrate to great depths and for the hydrocarbons to escape. The situation of naphtha at the foot of mountain chains is the chief argument in my hypothesis."[1]

According to this view, oil and gas are being *continuously generated*, for there is no reason to suppose that the masses of

[1] Mendeléeff: Principles of Chemistry, Vol. I, p. 365.

metallic carbides in the earth's interior are exhausted; such, in fact, seems to be Mendeléeff's view. He points especially to the absence of large quantities of nitrogen compounds in petroleum as an argument in favor of the hypothesis.

The objection has been urged against this hypothesis that petroleum, if thus produced, should be abundant in the primary rocks from which it is usually absent. The original heated condition of these rocks would have prevented the condensation of oil, however, and although the vapors may have passed through the earlier rocks, there is no reason to expect that condensation should have occurred before reaching much higher strata.

While on geological grounds difficult to prove or disprove, it meets with one fatal objection: the composition of natural gas in Pennsylvania does not justify the supposition that superheated steam and carbon have been concerned in its formation. We should certainly look, in such a case, to find natural gas composed mainly of free hydrogen containing small quantities of paraffins, olefines and carbon monoxide. When it is considered that paraffins alone cannot under any known circumstances be produced from the oxidation of carbide of iron by steam, the hypothesis does not seem to be tenable. It is true that varying conditions of temperature might have produced a great variety of hydrocarbons, but no evidence has yet been obtained that paraffins alone result from such a reaction. In an experiment made with ferromanganese and dilute sulphuric acid, the gas evolved was found to contain 6 per cent. of olefines.[1] It is further to be noticed that this hypothesis requires that water should take part in the process, yielding up its hydrogen, while, according to the older geological hypothesis, the water may have served mainly to cover and give protection from atmospheric oxidation, if it has been concerned at all in the reaction.

Water contains dissolved oxygen, and in descending to the iron carbides, must have given off its dissolved oxygen long before reaching the region at which actual formation of hydrocarbons could occur. Hence, on this hypothesis, oxygen should be found in natural gas in larger quantity than the chemical tests indicate. In fact, in rocks of moderately high conducting power, a wide interval would exist between the depth at which water

[1] Experiments by F. C. P.

boils and the much greater depth at which water-vapor could oxidize metallic iron in quantity. It is doubtful whether water could have traversed this interval so as to reach the latter depth at all.

Engler[1] has published the results of interesting investigations upon the distillation-products of menhaden fish-oil. By conducting the distillation at a high pressure (25 atmospheres), this author produced a mixture of hydrocarbon oils from which a large number of normal paraffins was obtained, compounds not found elsewhere in nature than in petroleum. This has led to the revival of an older theory as to the origin of petroleum and gas, *i. e.* that they have resulted from the distillation under pressure and at low temperatures of the accumulated remains of marine life buried under the sediments of the ancient Devonian seas.

Much has been written in support of the hypothesis of Engler, and it may be said to have gained very general acceptance in Europe. Ochsenius[2] has summarized many of the arguments usually adduced in support of the hypothesis:

This author says, "Concerning the origin of petroleum there is now no doubt that, with a few exceptions, animal remains (mainly of marine life) have yielded the raw material."

Originally the opinion was held that it was derived from vegetable matters, because the accumulation of animal remains sufficient to account for its formation by any distillation-process in the rocks could not be explained. Distillation of vegetable matters would, however, have left greater deposits of coal (as a residue in the Devonian rocks). But petroleum occurs in rocks of marine formation where coal is uncommon. Rocks in which plant remains are found do not contain bitumen (petroleum). If animal remains are associated with those of plants, then bitumen is usually found. The objection urged against the hypothesis of Engler, that nitrogen does not occur in petroleum, is easily overcome by the fact that the nitrogen of animal tissues tends finally to produce ammonia, and this in the case of petroleum may have been carried away in solution by water; hence the absence of nitrogen compounds.

From Engler's experiments it appears that animal fats are the chief source of petroleum.

[1] Ber. d. chem. Ges. **21**, 1816 (1888); **22**, 592 (1889). [2] Chem. Ztg. 1891, 936.

It is true that fatty matters do not ordinarily sink in water, although Von Guembel, in the voyage of the *Gazelle*, found fat globules in dredgings from the bottom of the Atlantic Ocean, in water 15,000 feet deep.

Putrefactive changes would tend to yield considerable quantities of ammonia and carbon dioxide. These in presence of salt water would produce alkali bicarbonate and ammonium chloride. Hence, alkaline waters might be looked for in the neighborhood of petroleum. The petroleum at Pechelbronn is associated with water containing 0.5 per cent. of alkaline carbonate.[1] Such alkaline waters are not known in archæan rocks, and are not, therefore, likely to be derived from greater depths than the rocks in which they are found. Probably no cases can be cited where fatty tissues alone of buried animals have yielded oil or gas. The presence of strongly saline water is apparently needed.

Great differences occur in the chemical character of petroleum. Caucasian oils are mainly composed of olefines or substances related to the olefine group. The German oils are mixtures of paraffins and olefines, while the American are chiefly paraffins. Such differences may be attributed to the character of the rock in which the distillation has occurred. Sandstones would probably prove without action; while limestones, by reason of their basic character, would tend strongly to influence the products.

Such are some of the arguments of Ochsenius in favor of Engler's hypothesis.

If this view is accepted, it follows that the generation of petroleum and gas must be considered as a finished process, so far as all existing productive gas and oil regions are concerned.

Engler has analyzed[2] the gas evolved (1) when menhaden oil and (2) when oleic acid is distilled (*a*) under atmospheric pressure and (*b*) under a pressure of 25 atmospheres.

	Menhaden Oil.		Oleic Acid.	
	1 atmos.	25 atmos.	1 atmos.	25 atmos.
Methane	25.2	38.3	9.3	4.36
Olefines	11.4	7.8	12.5	2.9
Carbon dioxide	26.7	17.4	37.2	26.0
Carbon monoxide	34.9	34.5	38.6	25.5
Incombustible residue,	1.8	2.0	2.4	2.0

[1] In Western Pennsylvania many cases are known of water having a decided alkaline reaction in the neighborhood of gas-wells. In the Murrysville gas territory, water of alkaline reaction was so abundant as seriously to interfere with gas development.—Note by F. C. P.

[2] Ber. d. chem. Ges. 22, 592 (1889).

The liquid distillates produced at the same time that these gases were evolved were rich in the normal paraffins and their isomers. 100 parts of menhaden oil yielded 8.9 parts of gas and 63 parts of liquid oils.

A strong argument in support of the Engler hypothesis is found in the fact that by distillation of fish-oils, besides methane, several of the lower paraffins are produced in large quantity. Hydrocarbons of the paraffin series are not obtainable in such proportions by the distillation at high temperatures of other organic material under ordinary conditions. It should be noted as a fact of much interest as regards the results of Engler's researches, that in the distillation at higher pressures the proportion of olefines contained in the gases evolved is considerably less. This is also true of carbon monoxide when oleic acid was distilled. It is to be regretted that Engler's experiments were not repeated at still higher pressures, in order to ascertain whether these same constituents of the evolved gases diminish progressively with increased pressure.

Engler was the first to show clearly that the problem of the origin of oil and gas must be studied from the chemical rather than the geological standpoint. The hypothesis advanced by this author has been very generally accepted. Nevertheless, my examinations of natural gas have led me to doubt some of his conclusions, well founded as they seem. The most careful tests, carried on during a period of six years, have failed to show the presence of either olefines or carbon monoxide in the natural gas of Western Pennsylvania.

Some of the constituents of gas are soluble in water. This is notably the case with carbon dioxide, butane, hexane, etc. If ethylene and carbon monoxide have been produced in the rocks even in much smaller proportion than Engler finds in menhaden-oil gas, these substances would now occur in the natural gas of Pennsylvania. Ethylene would give to the gas such illuminating power that there would be no occasion for the use of coal-gas in any town in the Western Pennsylvania gas-region. As a matter of fact, natural gas is almost useless as an illuminant, its light being equal to 5 to 11 candles per five feet of gas consumed per hour. Mr. Robert McKinney, formerly gas inspector of Allegheny county, found as a mean of forty trials of natural gas supplied to Pittsburgh an illuminating power of 6.5 candles. Mr. J. W.

Patterson, the present gas inspector of the county, states that the illuminating power of natural gas as supplied to Pittsburgh in November, 1892, is a little less than 11 candles per five feet per hour. The reason for this is that natural gas, as found in Pennsylvania, does not contain olefines. If carbon monoxide occurred in gas there would have been innumerable cases of poisoning among workmen at gas-wells. It is common to find such leaks of gas about the majority of gas-wells that no one could strike fire at a well without risk of fatal consequences. Although inhaling the escaping gas for much of a lifetime, a gas-well driller will usually maintain that no bad effects to health come from exposure to the gas. Air containing 0.2 per cent. of carbon monoxide is known to produce dangerous effects upon health. According to Wyss,[1] air containing 0.1 per cent. of water-gas is poisonous to breathe.

It is hardly probable, moreover, that carbon monoxide or ethylene occurring in gas could have been absorbed or removed at low temperatures by any natural process in the rocks. Unlike carbon dioxide and ammonia, their slight solubility in water would preclude the supposition that they had been dissolved away. Muck[2] cites analyses of fifty-seven samples of gas from coal mines and of gas occluded in coal. In only one case is carbon monoxide mentioned, but it is distinctly stated that its occurrence was not proved. Ethylene is mentioned in six cases, but Muck states that more recent analyses have failed to demonstrate its presence usually in gas from coal. The absence of hydrogen in all the analyses is especially noticeable. In the case of gases from the Caspian region, the presence of ethylene and carbon monoxide is to be anticipated, as, from all accounts, subterranean heat has been concerned in their production.[3]

[1] Ztschr. ang. Chem. 1888, p. 465.

[2] Grundzüge und Ziele der Steinkohlenchemie (1881).

[3] Constituents.	1.	2.	3.	4.	5.	6.	7.	8.
Carbon monoxide.....	0	0	0	0	0	0	0	0
Carbon dioxide.....	0.95	2.28	3.50	0	2.47	4.44	0	0.3
Olefines	4.11	3.26	4.26	0	0	0	0	..
Methane	92.49	93.07	92.24	95.39	97.57	95.56	1.90	..
Hydrogen.....	0.94	0.98	0	0	0	0	0	..
Nitrogen..... ..	2.13	0.49	..	..	..	..	96.57	96.8
Oxygen.....	..	..	..	..	..	..	1.53	2.9
	100.62	99.98	100.00	..	100.04	100.00	100.00	100.00

Nos. 1, 2, 3, 4, 5 and 6: natural gas from the Caspian region. Communicated by letter from Mr. M. Beliamin of Nobel Bros., St. Petersburg. No. 4 is the result of a partial analysis. Nos. 7 and 8, gas obtained by deep borings at Middlesborough, England (Bedson: J. Soc. Chem. Ind. **7**, 662 (1888)).

Thomas[1] gives analyses of fourteen samples of gas occluded by coal, and also of gas from blowers in coal mines in New South Wales. The analyses showed the presence of methane, nitrogen, carbon dioxide and oxygen; but no carbon monoxide, hydrogen or ethylene was found. Franke[2] gives analyses of mine-gases, according to which only carbon dioxide and methane were found. Winkler[3] found no hydrogen in nine samples of mine-gas. Many similar statements might be cited, all tending to prove that hydrogen, ethylene and carbon monoxide do not occur in gases occluded in coal.

The occurrence of gas consisting of nearly pure nitrogen, such as that obtained at Middlesborough, England[1]—in a region therefore where gas similar to Pennsylvania natural gas might be looked for—may perhaps be explained by the action of subterranean water upon deposits of coal or bituminous shale. The dissolved air in such waters, by causing slow oxidation, might lead to the production of carbon dioxide and the consequent removal of oxygen from the water. The carbon dioxide produced would lessen the solubility of the water for nitrogen, by causing the water to dissolve carbonate of lime, etc. Gentle heat from below would tend still further to the expulsion of the nitrogen, and thus a considerable but limited quantity of nitrogen might be obtained as a sudden outburst from a drill-hole.

It may be said that varying conditions of temperature and pressure, and kind of rock, have modified the products, so that perhaps the carbon monoxide and ethylene resulting from a laboratory experiment have, in nature's workshop, given place to paraffins. But, if the chemistry of the reaction supposed to occur is to be considered at all, the fact that distillation-experiments have produced from fish-oil certain bodies found in natural gas (paraffins) should not count more forcibly as geological evidence than the other fact that such distillation yields bodies which are foreign to natural gas as usually found in Pennsylvania.

I have failed to find any data tending to show that organic matter can be subjected to destructive distillation in such a manner as not to yield carbon monoxide and considerable quantities of olefines, together with hydrocarbons of still less saturated character. As a rule, the acetylenes and members of the benzene series appear.

[1] Watts' Dic. (1st Ed.), 3d Suppl. 529. [2] J. prakt. Chem. [2] **37**, 91, 113 (1888).
[3] Jsb. 1882, 1063.

Engler's hypothesis involves the supposition that a process of distillation has occurred at moderately high temperatures and at pressures measured by great depth of rock-strata. The carbon dioxide evolved in this destructive distillation must have come continuously into contact with the vast quantities of carbon which in its various stages of transformation from vegetable tissue to anthracite is so widely distributed throughout the rocks. The reaction $CO_2 + C = 2CO$, which proceeds rapidly at a strong heat and also slowly at lower temperatures, would then probably have occurred wherever the temperature was sufficiently high.

Prolonged contact of carbon dioxide with the carbonaceous residue of the distillation would perhaps be sufficient to increase considerably the final yield of carbon monoxide. According to I. L. Bell,[1] the reduction of carbon dioxide to carbon monoxide by carbon in the form of soft coke begins at 427° C. This is about the temperature at which Engler's distillation-experiments were conducted (360°–420° C.).

Engler has shown that distillation of animal fats at very high pressure (25 atmospheres) may yield gas containing less of carbon monoxide and olefines than when the process is conducted under atmospheric pressure. No data are at hand as to results at still higher pressure. If it is conceded that the proportion of carbon monoxide and ethylene in the gas evolved during destructive distillation decreases progressively with increase of pressure, and that these two constituents vanish altogether at sufficiently high pressures, it would still seem necessary to suppose that the pressure must have been at least twice as great when the process occurred in the rocks, as in the case of Engler's experiments. Taking the specific gravity of the rocks to be about 2½, it may be assumed that twelve feet of rock-strata represent a pressure of one atmosphere; six hundred feet of solid rock would then be required to produce a pressure of 50 atmospheres. This would be considerably less than the depth of the same quantity of rock material in the form of loose sediment before its consolidation. No case can be cited in recent times where sediment six hundred feet deep has been so suddenly accumulated as to bury unchanged the vast quantities of animal remains necessary to account for the production of oil and gas upon Engler's hypothesis, that oil and gas have

[1] Chemical Principles of the Manufacture of Iron and Steel, p. 101.

resulted from the action of pressure and moderate heat upon animal matters.

There is probably no reason to suppose that the gaseous olefines have, under the influence of pressure, given place to others of higher boiling-point by a process of polymerization. Should the possibility of such a change be proved, the absence of olefines from natural gas and their presence in petroleum might be explained. The possibility of secondary reactions among the constituents of a complex gas-mixture at high temperatures and under pressure adds difficulty to the problem, and caution is needed to avoid the error of overestimating the importance of any given reaction. It is generally true, however, that under such conditions secondary changes are probable, and that unsaturated compounds—olefines, acetylenes, carbon monoxide—are likely to result, especially when water-vapor and carbon dioxide are present.

It is a well-known fact that when petroleum is distilled, considerable quantities of unsaturated hydrocarbons are produced which did not exist in the original crude oil. This is shown by the bromine-absorption of the different products. The process of "cracking" or breaking-up by heat of the hydrocarbons in petroleum into simpler and less saturated compounds is familiar to all oil-refiners. Chemically speaking, "cracking" means the production of unsaturated hydrocarbons.

The fact that Engler has, in his extremely interesting and important researches, produced by distillation of animal matters so great a variety of paraffins constitutes by far the strongest argument in favor of his hypothesis.

Sorge, in an article which has been reproduced in numerous journals,[1] has stated that a strong resemblance exists between Pennsylvania natural gas and gas manufactured from Westphalian coal. Similarity in composition between natural gas and coal-gas would greatly simplify the problem of origin, and the fact of such similarity would prove of great interest. In this connection the following analysis of gas from Westphalian coal, carried out in the laboratory of the Westphalian Berggewerkschaftskasse in Bochum, will be of interest. I am indebted to Mr. Bergassessor E. Krabler, of Bochum, for the figures which he has kindly communicated by letter.

[1] *Stahl und Eisen*, **7**, 93; Jahrb. Min. 1887, **2**, Ref. 318; J. Chem. Soc. **54**, 31 (1888).

	1.	2.
Hydrocarbons, C_xH_y	5	4
Methane	45	35
Hydrogen	40	50
Carbon monoxide	5	5
Carbon dioxide	1	3
Nitrogen	4	3

The large percentage of hydrogen and the proportion of carbon monoxide in this gas illustrate at once the results of high temperature in the production of the coal-gas, but a similarity between this coal-gas and natural gas can hardly be said to exist.

When vegetable remains are buried under water, as is well known, decomposition occurs, yielding gas in considerable quantity. Tappeiner[1] has studied the products of this change very exhaustively. Pure cellulose (filter-paper) was found, under the influence of a microbe which was supplied with nutritive fluids, to dissolve in water, yielding gas-mixtures of two different types.

	Under water of neutral reaction.		Under slightly alkaline water.
	At beginning.	At end.	
Carbon dioxide Hydrogen sulphide	85.48	76.98	55.39
Hydrogen	0.0	0.0	42.71
Methane	11.86	23.01	0.0
Nitrogen	2.73	0.0	1.90

From these experiments it appears that, by the action of a microbe, either methane and carbon dioxide (neutral fluid), or hydrogen and carbon dioxide (alkaline fluid) may result. Hoppe-Seyler[2] found that gas evolved in the decay of cellulose under the influence of a microbe (marsh-gas fermentation) contained:

Carbon dioxide	50
Methane	45
Hydrogen	4

Popoff finds in a gas from decaying vegetable matters:

Marsh gas	68.56
Carbon dioxide	31.44

Berthelot states that hydrogen is produced in the vinous fermentation of mannite. In very careful experiments which I have

[1] Ber. d. chem. Ges. **16**, 1734 (1883). [2] *Ibid.* **16**, 122 (1883).

tried I have failed to find hydrogen in the gas evolved during the fermentation of 200 grams of sugar. Chemical changes of this type are not likely to be of importance, however, as regards the hydrogen question.

Gases from Sea-weeds.

The following experiments were tried in order to study the nature of the gases evolved in the decay of sea-weeds: A quantity of a large fucus kind from Santa Barbara, California, was used. 50 grams of the air-dried plant were soaked in water and then introduced into a flask filled with water, which had been previously boiled (in order to expel air) and cooled. The flask was connected with a bell-jar over a mercury-trough. After setting up the apparatus, no gas appeared until the third day; then a strong evolution of gas began and continued in slowly diminishing quantity for ten days, when the process ceased. In all, 803 cc. of gas were collected. Analyses were made (1) of the first portion of 300 cc. and (2) of a second portion of 300 cc., and (3) of the last portion of 203 cc. The results are tabulated below:

	First Portion.	Second Portion.	Third Portion.
Carbon dioxide	18.23	32.47	53.44
Carbon monoxide	...	...	...
Ethylene	...	...	...
Methane	.30	.28	.08
Hydrogen	62.24	48.97	42.02
Nitrogen	19.23	18.28	4.46
	100.00	100.00	100.00

Carbon dioxide was determined by soda solution over mercury; hydrogen by palladium asbestos, using a Hempel apparatus. The absence of carbon monoxide and ethylene was proved by palladium-chloride solution. Methane was determined by combustion with air, using a red-hot platinum tube. The carbon dioxide produced in the combustion was absorbed by baryta solution of known strength, and the excess of baryta determined by standard oxalic acid. The following facts are of especial interest:

1. The carbon dioxide increases towards the end of the decay. 2. The hydrogen steadily diminishes. 3. Methane occurs only in traces. 4. Nitrogen occurs in such considerable quantity as to render it probable that this gas is set free in the process of decay.

The same apparatus was kept in position for two and a half years after the above experiments were finished. During that time a continuous production of gas was observed, but it was so slow that at the end of this period only about 30 cc. of gas collected. This was found to consist of methane.

I have examined the gases produced in swampy ground in many different places. Samples were taken from streams having muddy bottoms and in which vegetable matter had collected. Samples of gas have also been taken from salt marshes on the coast of Maine. Gas has also been collected from the very deep accumulations of mud and decaying vegetable remains found in some parts of Lake Chautauqua. The general result of examinations of these gas samples may be stated to the effect that the gas occurring in shallow swamps and streams consists of methane, carbon dioxide and nitrogen. In some of the much deeper swamp waters, where masses of vegetable débris of greater thickness are found (as in Lake Chautauqua), hydrogen occurs in very small quantity. Great difficulty is experienced in taking samples of gas from localities of the latter type. Tappeiner observes that the marsh-gas fermentation is probably a very important source of methane in nature.

The fact that buried vegetable matters may, after a brief period of rapid gas-evolution, pass into a condition of extremely slow decay, adds greater force to the original theory of petroleum and gas. The occurrence of so large a proportion of free hydrogen among the gases evolved by vegetation in process of decay is a matter of great interest, as it suggests the existence of an important source of hydrogen wherever deeply submerged plant-remains occur. Frankland and Jordan[1] found that grass left to decay under water (air being excluded) evolved in three days gas of the following composition:

Carbon dioxide,	84.63
Oxygen,	0.13
Hydrogen,	6.90
Other combustible gases,	2.51
Nitrogen,	5.83

Vegetable tissue, after the somewhat sudden and tumultuous evolution of gas, seems to be capable of relapsing into an

[1] J. Chem. Soc. **43**, 295 (1883).

extremely slow and long-continued process of decay. After the first decomposition, such remains might become accumulated and buried deeply under sediments before the tissues are materially altered. The generation of gas might then proceed in the cold. It seems hardly possible to ignore this probable source of natural gas in discussing any theory as to its origin, especially when it is considered that no other process in nature has been found to yield a gas at all similar in composition to that found in the rocks.

Of the three hypotheses which have been proposed to account for the production of oil and gas, two are open to a serious objection.

1.—The chemical changes supposed by Engler to have been the cause would probably yield gas different in composition from the natural gas now being obtained in such large quantity in Western Pennsylvania; and if the gas originally contained ethylene and carbon monoxide, it is not easy to explain their complete disappearance in the natural gas I have examined from wells scattered over so large a region.

2.—The hypothesis of Mendeléeff would be much more difficult to reconcile with the facts as regards composition. The total absence of hydrogen could not be easily explained. The only process in nature which is known to yield gas similar in its constituents to natural gas is that which occurs in swamps and decaying masses of submerged vegetable remains.

The important fact that the solid plant tissues may be preserved for long periods after the preliminary gas-evolution has ceased shows that the remains are likely to become slowly buried, to undergo the "fermentation" changes leading to the production of methane. Animal tissues can suffer no such arrest of decomposition. Decay once set in is carried rapidly onward to complete destruction without intermission. The contrast between the conditions in which animal and plant-remains occur in the rocks seems to justify this statement.

If chemical evidence shall count in the discussion, it is difficult to find a more satisfactory explanation than the older hypothesis which the geologists advanced, although in their treatment of the subject the strictly chemical arguments were neglected.

THE CONDENSATION-PRODUCTS OF AROMATIC HYDRAZIDES OF ACETACETIC ETHER.— INDOL AND PYRAZOL DERIVATIVES.

By C. Walker.

In a former paper I showed that the product of the reaction between acetacetic ether and concentrated sulphuric acid is ethylic α-methylindol-β-carboxylate.[1] With the permission of Dr. Nef, I have continued this work, applying the reactions to homologous compounds.

As considerable diversity of experience with acetacetic-ether phenylhydrazide has been recorded by different authors,[2] I shall briefly give my own experience in working with the hydrazides. In my earlier preparations of these substances, especially in the case of oxalacetic-ether phenylhydrazide, I experienced difficulty in preventing the splitting off of alcohol and consequent formation of pyrazolone. If instead of adding the hydrazine to the acetacetic ether the ester be added to the hydrazine, no pyrazolone is formed. Operating in this manner, only a very small volume of absolute ether is necessary, and in the preparation of all hydrazides except oxalacetic-ether hydrazide, the ester may be poured *slowly* into the hydrazone. When about half of the acetacetic ether (or substituted acetacetic ether) is added, a turbidity due to the separation of water is noticed. The addition of the ester is continued, accompanied by vigorous shaking all the while. The mixture should not be cooled. After standing 3 to 4 hours the water is removed by means of a separatory funnel, and the ethereal solution dried with calcic chloride or anhydrous sodic sulphate. This was the method by which all hydrazides experimented with were prepared, except when special purity was desired, as in the numerous attempts to obtain ethoxypyrazols from them by means of acetyl chloride. The hydrazides were then washed in ethereal solution with alkali and acid. Oxalacetic-ether phenylhydrazide cannot be washed in ethereal solution with dilute sodic hydrate (1 : 20) without almost complete conversion into pyrazolone. All other hydrazides, however, can be thus treated with only partial conversion into pyrazolone. All of the

[1] This Journal **14**, 576. [2] *Ibid.* **14**, 516.

hydrazides (including oxalacetic hydrazide) can be washed in ether solution with dilute sulphuric acid with only a slight formation of pyrazolone. The tolylhydrazides are much more stable towards alkalies than phenylhydrazide. That the hydrazides are purer when washed with alkali and acid is shown by the following observations, which were often made. The washed and unwashed hydrazide were placed side by side in the same desiccator; after a few days' standing the unwashed hydrazide was almost completely changed into pyrazolone, while the washed hydrazide resisted this change for some weeks.

In their deportment towards concentrated sulphuric acid the hydrazides have been found to behave quite differently. Acetacetic-ether phenylhydrazide when treated with strong sulphuric acid at low temperatures gives an indol derivative; acetacetic-ether orthotolylhydrazide and acetacetic-ether paratolylhydrazide also lose ammonia, giving indol bodies; methyl- and benzylacetacetic-ether phenylhydrazides, when similarly treated, give pyrazolonesulphonic acids; ethylacetacetic-ether phenylhydrazide, under the same treatment, loses ethylamine, with consequent formation of an indol derivative; while oxalacetic-ether phenylhydrazide loses water and gives rise to an ethoxypyrazol. The different compounds obtained will be described in the order of indol, pyrazol and pyrazolone derivatives.

I.—Indol Derivatives.

Ethylic paratolyl-α-methylindol-β-carboxylate.—The acetacetic-ether paratolylhydrazide from which this body is derived, was prepared by the method already indicated, *viz.* by adding acetacetic ether to paratolylhydrazine partly dissolved in a small volume of absolute ether. The oily hydrazide was dropped slowly into about five volumes of concentrated sulphuric acid at —15°. Not more than 10 grams of the hydrazide should be used in one operation. After standing 10–15 minutes the sulphuric-acid solution was poured slowly upon ice contained in a funnel, the drippings being received in a beaker containing ice. The solution was then extracted with ether, the ethereal solution washed repeatedly with alkali and dried with calcic chloride. The yield of indolcarboxylic ester was a little less than 30 per cent. After recrystallizing from dilute alcohol and drying over sulphuric acid in a vacuum, it was analyzed:

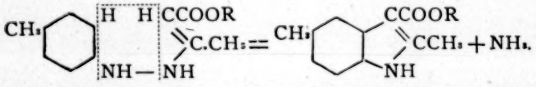
I. 0.1475 gram substance gave 0.3877 gram CO_2 and 0.0917 gram H_2O.

II. 0.2171 gram substance gave 0.5692 gram CO_2.

III. 0.1797 gram substance gave 10.5 cc. N at 23° and 757.5 mm.

	Theory for $C_{13}H_{15}NO_2$.	Found. I.	II.	III.
C	71.88	71.69	71.50	...
H	6.91	6.90	6.96	...
N	6.45	...	...	6.71

The acetacetic-ether paratolylhydrazide, therefore, has lost one molecule of ammonia; that the splitting off of ammonia has taken place in precisely the same manner as in the case of acetacetic-ether phenylhydrazide when similarly treated will appear presently:



Ethylic paratolyl-α-methylindol-β-carboxylate (or B3, Pr2-dimethylindol-Pr3-carboxylate) crystallizes from dilute alcohol in regular octahedra and tetrahedra melting at 163°–163.5° without decomposition. It is readily soluble in alcohol, ether, benzene and acetone. Like the indol derivative from phenylhydrazide, it gives the indol splinter-reaction. It is very stable towards alcoholic caustic potash: 0.4 gram was heated with an excess of potash with return-cooler two days without change. It can be heated in a sealed tube with a slight excess of alcoholic caustic potash at 125°–130° for several hours without undergoing change. Heated, however, at 150° with a little less than an equal weight of potassic hydrate dissolved in alcohol, it is saponified. The alcoholic solution, after being filtered from the potassic carbonate which had separated, was evaporated to dryness and the oil thus obtained was finally crystallized from dilute alcohol. This indol derivative melted at 112°–114°, and agreed in all its properties with B3, Pr2-dimethylindol obtained by Raschen.[1] As a further means of identification a nitrogen determination was made:

0.1401 gram substance gave 12.2 cc. N at 20° and 750 mm.

[1] Ann. Chem. (Liebig) **239**, 227.

	Calculated for $C_{16}H_{11}N$.	Found.
N	9.66	10.04

Ethylic orthotolyl-α-methylindol-β-carboxylate. — Acetacetic-ether orthotolylhydrazide was prepared in the usual manner and purified by crystallizing from ligroïn. It melts at 95°–97°. It is readily soluble in all organic solvents. Like the corresponding para compound, it is more stable toward alkalies than the phenylhydrazide. It may be kept in a vacuum-desiccator for weeks without change.

The hydrazide was converted into the indolcarboxylic ether by treating with strong sulphuric acid, pouring upon ice, etc., as in the case of the para compound. The yield of indol was a little less than that from the paratolylhydrazide, being about 22 per cent. After recrystallizing from dilute alcohol and drying in a desiccator it was analyzed.

I. 0.2648 gram substance gave 0.6921 gram CO_2 and 0.1744 gram H_2O.

II. 0.1985 gram substance gave 0.5227 gram CO_2 and 0.1261 gram H_2O.

III. 0.2438 gram substance gave 14.0 cc. N at 20° and 749.8 mm.

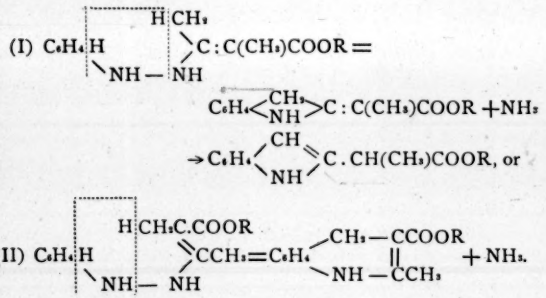
	Theory for $C_{13}H_{15}NO_2$.	Found. I.	II.	III.
C	71.88	71.28	71.78	...
H	6.91	7.30	7.05	...
N	6.45	...	...	6.57

From the analyses and the previous results with acetacetic-ether phenylhydrazide and acetacetic-ether orthotolylhydrazide, there can be no doubt that the orthotolylhydrazide, by treatment with concentrated sulphuric acid, has lost ammonia in a similar manner, giving B1, Pr2-dimethylindol-β-carboxylic ester, so that the conversion of the ortho-carboxylic indol into the corresponding dimethylindol derivative by saponifying and simultaneous splitting off of carbon dioxide was not considered necessary.

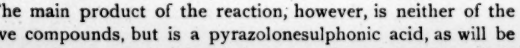
Ethylic orthotolyl-α-methylindol-β-carboxylate crystallizes from dilute alcohol in prisms belonging to the monoclinic system. It melts at 173° without decomposition (remelting at the same temperature). It is readily soluble in ether and alcohol.

Indols from the Substituted Acetacetic Ethers.—It was next attempted to obtain indol derivatives from the substituted acetacetic ethers by the method above employed. The alkyl acet-

acetic ethers experimented with were methyl-, ethyl- and benzyl-acetacetic ether. The methylacetacetic ether used was prepared according to the method of Conrad and Limpach.[1] It boiled at 195°–197° under ordinary pressure with only slight decomposition. It reacts with phenylhydrazine much less readily than any of the substituted acetacetic ethers experimented with, so that in preparing the hydrazide the whole of the methylacetacetic ether may be added at once to the phenylhydrazine in absolute ether. The mixture may be heated on the water-bath at 50°–60° for several hours without danger of converting into pyrazolone, or it may be allowed to stand twelve hours at the ordinary temperature, when the reaction is complete. After drying the ethereal solution with calcic chloride and evaporating off the ether completely, the hydrazide was treated with concentrated sulphuric acid in the usual manner. This hydrazide may lose one molecule of ammonia in two different ways:



The main product of the reaction, however, is neither of the above compounds, but is a pyrazolonesulphonic acid, as will be shown under the section devoted to pyrazolone derivatives. But reaction I. was also shown to take place at the same time, giving



This compound was found in the ethereal extract of the products of the reaction. After washing the ether solution with alkali, drying and evaporating off the ether, there remained an oil, part

[1] Ann. Chem. (Liebig) **192**, 153.

of which was made to solidify. The solid portion was separated from the oil by absorbing the latter in clay plates. After recrystallizing the solid substance from dilute alcohol and drying in a desiccator, it was analyzed.

I. 0.1120 gram substance gave 0.2926 gram CO_2 and 0.0710 gram H_2O.

II. 0.1323 gram substance gave 0.3471 gram CO_2 and 0.0867 gram H_2O.

III. 0.1930 gram substance gave 11.0 cc. N at 24° and 754 mm.

	Theory for $C_{13}H_{15}NO_2$.	Found. I.	II.	III.
C	71.88	71.34	71.55	...
H	6.91	7.04	7.28	...
N	6.45	...	...	6.50

α-Indolpropionic ether, or methylindolacetic ether, separates from dilute alcohol in white crystals melting at 136°. It is readily soluble in organic solvents and gives the indol splinter-reaction. By saponification and splitting off of carbon dioxide it should yield *α*-ethylindol, but for lack of sufficient substance this experiment could not be made.

Ethylic α-methylindol-β-carboxylate from ethylacetacetic-ether hydrazide.—When ethylacetacetic-ether phenylhydrazide is treated with strong sulphuric acid at —12° a faint aromatic odor is observed.[1] The ethereal extract, obtained by the usual method, after being washed with alkali contained an indol derivative which melted at 131° and in all its properties agreed with the indol obtained from acetacetic-ether hydrazide by similar treatment. After crystallizing from dilute alcohol and drying in a desiccator it was analyzed.

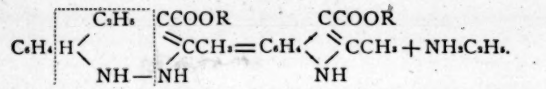
I. 0.1670 gram substance gave 0.4291 gram CO_2 and 0.0990 gram H_2O.

II. 0.2030 gram substance gave 13.1 cc. N at 24° and 750 mm.

	Theory for $C_{13}H_{13}N_3O$.	Found. 1.	II.
C	70.90	70.77	...
H	6.40	6.57	...
N	6.90	...	7.30

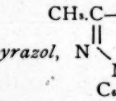
The formation of ethylic *α*-methylindol-*β*-carboxylate from ethylacetacetic-ether hydrazide necessitates the splitting off of ethyl amine:

[1] The ethylacetacetic ether used was obtained of Kahlbaum.

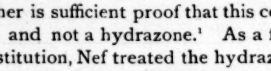


The mechanism of the reaction, therefore, between ethylacetacetic-ether phenylhydrazide and sulphuric acid is quite different from that of the other indol reactions studied.

II.—Pyrazol Derivatives.



1-Phenyl-3-methyl-5-ethoxypyrazol, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} C(CH_3)=CH \\ \| \quad \| \\ N \quad C(OC_2H_5) \end{smallmatrix}$, C_6H_5. — The fact that the condensation-product of acetacetic ether and phenylhydrazone by oxidation with mercuric oxide gives phenyl-β-azocrotonic ether is sufficient proof that this condensation-product is a hydrazide and not a hydrazone.[1] As a further proof of the hydrazide constitution, Nef treated the hydrazide in ethereal solution with an excess of acetyl chloride, and the oil thus obtained was supposed to be a diacetyl derivative of the hydrazide:



thus further proving the presence of two imido groups in the hydrazide. In view of the results obtained with oxalacetic-ether hydrazide,[2] and the high percentage of carbon found by Nef in the supposed diacetyl derivative (two per cent. more than that required by theory),[3] it seemed highly probable that acetyl chloride had acted on the hydrazide as a dehydrating agent, with the formation of an ethoxypyrazol. This supposition has been confirmed by experiment, but it will also presently appear that acetyl derivatives of the hydrazides are formed at the same time. Freer has more recently treated acetacetic-ether phenylhydrazide with acetyl chloride,[4] but his results are wholly different from my own.

The isolation of the ethoxypyrazol was at first attended with considerable difficulty; I was formerly able to prove its existence only by means of its platinum double salt.[5] Various dehydrating

[1] Ann. Chem (Liebig) **266**, 74. [2] This Journal **14**, 576.
[3] Ann. Chem. (Liebig) **266**, 76. [4] This Journal **14**, 517. [5] *Ibid.* **14**, 585.

agents have been employed to split off water from acetacetic-ether hydrazide. Acetyl chloride has been found most effective in accomplishing this. Zinc chloride, phosphorus pentoxide and acid potassium sulphate have been tried with negative results. Dry hydrochloric-acid gas passed into a glacial acetic-acid solution of the hydrazide (as in the case of oxalacetic-ether hydrazide),[1] gave the desired result, but the yield is much better when acetyl chloride is used. After various modifications, the following method was found most satisfactory:

To 4 or 5 grams of the hydrazide dissolved in 50–60 cc. absolute ether, well cooled by salt and ice (—15°), is slowly added an equal weight of freshly distilled acetyl chloride with constant shaking. The ether solution sometimes becomes turbid, at other times it remains perfectly clear; in either case the yield of ethoxypyrazol is the same. After standing a few minutes at ordinary temperature, an oil separates at the bottom of the flask. The mixture is then heated a short time on the water-bath at 50°–60°, and afterwards diluted with water. The ether solution, after washing thoroughly with acid and alkali, is dried with calcic chloride. Upon evaporating off the ether the ethoxypyrazol remains in the form of yellow needles.

If in the above preparation, after the addition of acetyl chloride, the mixture is not heated but is poured on ice at once and subsequently treated as described, the yield of oil is quantitative,—frequently it is more than quantitative, especially in the treatment of acetacetic-ether orthotolylhydrazide—a sufficient indication of the formation of acetyl derivatives. In this case the ethoxypyrazol may be separated from the oil by one of two methods: (1) by distilling under diminished pressure, or (2) by allowing the oil to stand twelve hours with concentrated hydrochloric acid to decompose any unchanged hydrazide or acetyl derivatives that may be present. Of these two methods the latter is to be preferred. After treatment with hydrochloric acid the products are taken up with ether, washed with alkali, etc., as above.

The average yield of the ethoxypyrazol was little less than one gram from four grams of the hydrazide; if two or three times this amount of hydrazide be used in an operation the yield is not increased. After recrystallizing from dilute alcohol and drying in a desiccator it was analyzed.

[1] This Journal **14**, 580.

I. 0.1541 gram substance gave 0.4007 gram CO_2 and 0.0931 gram H_2O.

II. 0.2040 gram substance gave 0.5306 gram CO_2 and 0.1230 gram H_2O.

III. 0.3173 gram substance gave 39.8 cc. N at 23° and 745 mm.

IV. 0.2740 gram substance gave 34.0 cc. N at 20° and 745 mm.

	Theory for $C_{12}H_{14}N_2O$.	Found. I.	II.	III.	IV.
C	71.28	70.91	70.93	...	...
H	6.93	6.71	6.69	...	...
N	13.86	...	...	14.17	14.21

1-phenyl-3-methyl-5-ethoxypyrazol is insoluble in water, but readily soluble in all organic solvents. It crystallizes from petroleum ether, at first in yellow six-sided prisms, finally in needles which are slightly yellow. Although this method of purifying is a slow one, the ease with which the pyrazol separates is quite remarkable; when the last trace of solvent has evaporated on standing, the whole of the ethoxypyrazol remains in crystalline form. In this way prisms fully two centimeters in length were obtained. It is most easily purified by crystallizing from dilute alcohol, from which it separates in white needles melting at 68°–68.5°. In alcoholic solution with ferric chloride it gives no coloration. It shows Knorr's "pyrazolin-reaction," giving a bluish-green coloration, which was permanent after sixty hours standing. Its platinum double salt has already been described.[1] When heated for 2–3 hours with one-and-a-half times the calculated amount of alcoholic caustic potash, phenylmethylethoxypyrazol is quantitatively saponified into

1-*Phenyl*-3-*methyl*-5-*oxypyrazol.*—Unlike the ester from which it was derived, this body dissolves readily in alkali hydroxide or carbonate, from which solution it is reprecipitated by mineral acids. After crystallizing from dilute alcohol and drying at 110° it was analyzed.

I. 0.1909 gram substance gave 0.4801 gram CO_2 and 0.0973 gram H_2O.

II. 0.2246 gram substance gave 0.5662 gram CO_2 and 0.1163 gram H_2O.

III. 0.1322 gram substance gave 19.0 cc. N at 27° and 745 mm.

[1] This Journal **14**, 585.

	Theory for $C_{10}H_{10}N_2O$.	Found. I.	II.	III.
C	68.96	68.59	68.75	...
H	5.75	5.66	5.78	...
N	16.09	...	...	15.96

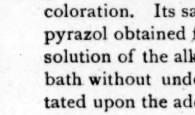
Phenylmethyloxypyrazol (1, 3, 5) is readily soluble in all organic solvents: ether, alcohol, benzene, ligroïn, chloroform and acetic ether were tried. It separates from benzene solution at first in flat plates, later in needles. It is best purified by crystallizing from dilute alcohol, from which it separates in orange-yellow needles, melting at 196°–198° with decomposition. An alcoholic solution with ferric chloride gave no coloration. It gives Knorr's "pyrazolin-reaction," giving a permanent green coloration. Its salts are far more stable than those of the oxypyrazol obtained from oxalacetic-ether hydrazide.[1] The aqueous solution of the alkali salts can be heated for hours on the water-bath without undergoing change, the oxypyrazol being precipitated upon the addition of an acid. It forms calcium and barium salts which are quite readily soluble in water, but unfortunately they were lost by the collapse of a vacuum-desiccator while concentrating their aqueous solution. A silver salt, however, was made from the neutral ammonium salt in the usual manner, and after thoroughly drying, a determination of silver in the salt was made:

	Theory.	Found.
Ag	38.43	38.02

III.—Pyrazolone Derivatives.

It has already been stated that the chief products of the action of concentrated sulphuric acid on methyl- and benzylacetacetic-ether hydrazide are pyrazolonesulphonic-acid derivatives.

1-*Phenyl*-3,4-*dimethyl*-5-*pyrazolone*-2 *?-sulphonic acid*,[2]



.—Methylacetacetic-ether phenylhydrazide was treated with strong sulphuric acid at —15°. Upon pouring the

[1] This Journal **14**, 583.

[2] In these sulphonic-acid formulæ the sulphonic group is united to nitrogen; no experimental evidence, however, of the position of the sulphonic group is thus far known.

sulphuric-acid solution on ice, an odor very much like that of methylketol was observed; in the second preparation this odor was not perceptible until after the sulphuric-acid solution had stood a few hours. The solid product of the reaction (which proved to be the pyrazolonesulphonic acid) was filtered off and the filtrate extracted with ether as described on page 434. The relative yield of the three products of the action of sulphuric acid on methylacetacetic-ether hydrazide was: 12.0 grams of the hydrazide gave 7.0 grams crude sulphonic-acid derivative, 1.0 gram indol derivative, 2.1 grams oil of unknown composition. On treating the hydrazide with sulphuric acid at higher temperatures than —15° the yield of the pyrazolonesulphonic acid is diminished.

The brownish-colored sulphonic acid at first possessed a strong indol odor, due to adhering indol. Upon crystallizing from alcohol (95-per cent.) a few times, the odor of indol entirely disappeared. After drying in a vacuum-desiccator it was analyzed:

I. 0.1265 gram substance gave 0.2270 gram CO_2 and 0.0507 gram H_2O.

II. 0.1389 gram substance gave 0.2481 gram CO_2 and 0.0551 gram H_2O.

III. 0.2190 gram substance gave 18.9 cc. N at 24° and 754.1 mm.

IV. 0.1368 gram substance gave 0.1141 gram $BaSO_4$.

	Theory for $C_{11}H_{12}N_2SO_4$.	Found. I.	II.	III.	IV.
C	49.25	48.94	48.71	...	...
H	4.47	4.45	4.40	...	...
N	10.44	...	...	9.87	...
S	11.94	...	...	...	11.46

Phenyldimethylpyrazolonesulphonic acid separates from boiling water at first in gray, finally in perfectly white, needles. It is best purified from 95-per cent. alcohol, from which it separates in apparently short white needles. (The adhering indol should first be removed from the crude product by treating with a small amount of alcohol, in which the indol is much more readily soluble than the sulphonic acid.) It does not melt at 300° and is difficultly soluble in all solvents. It gives Knorr's "pyrazolin-reaction."

1-Phenyl-3-methyl-4-benzyl-5-pyrazolone-2?-sulphonic acid.— Benzylacetacetic-ether hydrazide was treated with strong sulphuric acid at about —15°. Upon pouring the mixture on ice a faint indol-like odor was observed, and a voluminous separation

of a brownish-colored solid took place. This was filtered off and the filtrate extracted with ether. The washing of the ether solution with dilute sodic hydrate removed nearly the whole of the coloring matter. After drying the ether solution with calcic chloride and evaporating off the ether there was left a very small amount of oil: from 14 grams of the hydrazide only 3–4 drops of oil were obtained. This oil possessed a strong indol odor and gave the indol splinter-reaction. The quantity obtained did not permit of further examination. By carrying out the reaction at temperatures above —15° the yield of this oil is increased.

The crude sulphonic acid is best purified by treating with a small volume of alcohol to dissolve adhering indol and then crystallizing from 95-per cent. alcohol. After repeated crystallizations and drying at 110°, it was analyzed.

I. 0.1206 gram substance gave 0.2607 gram CO_2 and 0.0520 gram H_2O.

II. 0.1111 gram substance gave 0.2415 gram CO_2 and 0.0476 gram H_2O.

III. 0.3309 gram substance gave 0.7183 gram CO_2 and 0.1455 gram H_2O.

IV. 0.2683 gram substance gave 18.7 cc. N at 20° and 742 mm.

V. 0.1755 gram substance gave 12.7 cc. N. at 19° and 742 mm.

VI. 0.1510 gram substance gave 0.1040 gram $BaSO_4$.

VII. 0.2104 gram substance gave 0.1401 gram $BaSO_4$.

	Theory for $C_{17}H_{18}N_2SO_4$.	Found. I.	II.	III.	IV.	V.	VI.	VII.
C	59.30	58.95	59.28	59.20	...	...	...	...
H	4.65	4.78	4.70	4.88	...	...	...	...
N	8.11	...	...	...	8.00	8.29	...	...
S	9.33	...	...	...	...	...	9.45	9.57

Analyses II and III were made with a mixture of lead chromate and potassium dichromate.

1-Phenyl-3-methyl-4-benzyl-5-pyrazolone-2-sulphonic acid crystallizes from alcohol in exceedingly light, white flakes. It does not melt at 300°. It is much more easily soluble in hot benzene and chloroform than in alcohol. It is more difficultly soluble in water than the sulphonic acid obtained from methylacetacetic ether hydrazide. It forms stable salts which could not be made to crystallize. It gives Knorr's "pyrazolin-reaction."

Attempts to split off the sulphonic group by heating with concentrated hydrochloric acid in sealed tubes were unsuccessful, part

of the substance being unchanged and the remaining portion undergoing total decomposition. Attempts to split off the sulphonic group by heating for some time on the water-bath with moderately strong sulphuric acid also failed.

Although all attempts to convert the sulphonic acid into the known phenylmethylbenzylpyrazolone were unsuccessful, that the body is a sulphonic derivative of phenylmethylbenzylpyrazolone was proved by direct synthesis: Phenylmethylbenzylpyrazolone was treated with concentrated sulphuric acid at —15° to —20° and the solid products of the reaction washed on clay plates with ether. On crystallizing from alcohol, two substances were obtained, one melting at 210° (perhaps an inden-derivative not further investigated), and a difficultly soluble substance not melting at 300°. The latter was identical with the sulphonic acid obtained from benzylacetacetic-ether hydrazide.

1-*Phenyl*-3-*methyl*-4-*benzyl*-5-*pyrazolone*.—This was obtained by the spontaneous decomposition of benzylacetacetic-ether hydrazide at the ordinary temperature. All unchanged hydrazide was removed by washing with ether, and the pyrazolone further purified by crystallizing from dilute alcohol. After drying in a desiccator it was analyzed:

I. 0.1277 gram substance gave 0.3628 gram CO_2 and 0.0731 gram H_2O.

II. 0.1345 gram substance gave 13.0 cc. N at 24° and 750 mm.

	Theory for $C_{17}H_{16}N_2O$.	Found. I.	II.
C	77.27	77.49	...
H	6.06	6.44	...
N	10.60	...	11.00

Phenylmethylbenzylpyrazolone (1, 3, 4, 5) separates from alcohol in glistening scales which melt at 136°. It is insoluble in ether, slightly soluble in boiling water, readily soluble in alkali, chloroform, acetone and acetic ether, less readily in benzene and ligroïn.

1-*Orthotolyl*-3-*methyl*-5-*pyrazolone*.—This compound was prepared from acetacetic-ether orthotolylhydrazide and purified by the same method as the benzylpyrazolone. It separates from alcohol at first in four-sided prisms, later in white needles which melt at 143°–144°. It is insoluble in ether, water, ligroïn and acetic ether, but slightly soluble in chloroform.

CHEMICAL LABORATORY, CLARK UNIVERSITY, *June*, 1893.

A SYSTEMATIC STUDY OF THE ACTION OF DEFINITELY RELATED CHEMICAL COMPOUNDS UPON ANIMALS.

By Wolcott Gibbs, M. D., *Rumford Professor (Emeritus) in Harvard University*, and Edward T. Reichert, M. D., *Professor of Physiology in the University of Pennsylvania.*

[*Continued from p.* 370, *Vol.* 13.]

Our study of the physiological actions of definitely related chemical compounds has been brought to a conclusion by want of funds, a large appropriation from the Bache fund and a smaller one from the Smithsonian Institution having been exhausted. The very extended programme of work must therefore be abandoned, though with the earnest hope that investigators will take up the subject from the same point of view, and that in future the study of isolated compounds will assume a subordinate place. It remains for us to discuss the results which have been obtained, and to draw from them such conclusions as may be warranted under the circumstances. These conclusions are not always positive on account of the limited number of cases to be considered. On the other hand, we hope to be able to show that negative conclusions may have a certain value.

Phenol.

In discussing compounds belonging to the aromatic series, it will be most convenient to start with phenol, C_6H_5OH, which has been studied with great care as regards its physiological actions. We cannot trace the changes in its actions produced by passing from benzol, C_6H_6, to phenol, by the replacement of an atom of hydrogen by a molecule of hydroxyl OH, but we have materials for discussing successive replacements in phenol as in the di- and triphenol derivatives, and we shall consider these first in order.

As phenol forms our term of comparison it will be well in this place to recapitulate the results which have been obtained by different investigators as to its physiological relations. It will be sufficient to state that it appears first to stimulate and then to depress the spinal centers. In sufficient quantity the drug depresses the heart and the vaso-motor centers, and thus reduces arterial pressure. Phenol in the first stages of its action increases

the frequency of respiration in a remarkable degree, partly from stimulation of the peripheral pulmonic vagi and partly from that of the respiratory centers. Finally, when injected into rabbits phenol produces a very distinct fall in the bodily temperature, usually but not always coincident with the lowering of the arterial pressure.

The formula of phenol is C_6H_5OH. By the replacement of a second atom of hydrogen we have $C_6H_4(OH)_2$, and under this general formula we have ortho, meta and para compounds which we may distinguish in the usual manner by writing the formulæ *o*-$C_6H_4(OH)_2$, *m*-$C_6H_4(OH)_2$, *p*-$C_6H_4(OH)_2$. The results of our study of these are as follows:

Ortho-dihydric phenol, or pyrocatechin, *o*-$C_6H_4(OH)_2$.—The action of this compound upon the system is, as we have shown, very much more powerful than that of phenol and differs from it by being exerted more energetically on the spinal centers. Convulsions are also produced by the action of phenol, but they are very much less marked, and it seems safe to say that the difference in the action of phenol and ortho-dihydric phenol is chiefly one of degree, and that the replacement of a second atom of hydrogen by a second molecule of hydroxyl results in the production of a more active agent of the same general character.

Meta-dihydric phenol, or resorcin, *m*-$C_6H_4(OH)_2$.—Making due allowance for its less powerful action, resorcin affects the system in a manner very similar to pyrocatechin. The same is true of hydroquinone, *p*-$C_6H_4(OH)_2$, which as regards intensity of action comes next to pyrocatechin and stands above resorcin.

In the cases of the two *trihydric phenols* studied, namely, *pyrogallol* (1, 2, 3) and *phloroglucin* (1, 3, 5), it appears that the characters of the actions upon the system do not essentially differ from those of phenol or the three dihydric phenols already cited. It is important to note that the intensity of the action of pyrogallol, 1, 2, 3-$C_6H_3(OH)_3$ is less than that of pyrocatechin or the ortho-dihydric phenol, and agrees very closely with that of hydroquinone when measured by experiments on dogs. The action of pyrogallol is very much more powerful than that of phloroglucin. This may be connected with the fact that pyrogallol possesses a very high reducing power or, better, a very strong affinity for oxygen, and in the same connection we may note that pyrocatechin, like pyrogallol, reduces cold solutions of silver, while

the (physiologically) less active resorcin reduces silver salts only on boiling.

The third trihydric phenol, or *oxyhydroquinone* (1, 2, 4) should also be studied. We have not been able to procure it for our work. The three tetroxybenzols, $C_6H_2(OH)_4$, (1, 2, 4, 5; 1, 3, 4, 5; and 1, 2, 3, 4), as well as the hexoxybenzol, $C_6(OH)_6$, also deserve study, as does the large group of phenols of other types. With respect to the function of the molecule OH in these compounds it may be remarked that solutions of hydroxyl according to recent experiments are not toxic when taken into the stomach. We have, further, abundant evidence to show that it is not toxic in inorganic acids, as, for example, in sulphuric acid, $SO_2(OH)_2$, nitric acid, NO_2OH, metaphosphoric acid, PO_2OH, phosphoric acid, $PO(OH)_3$, etc. On the other hand Brunton, Bohenham, and others have shown that hydroxylamine, NH_2OH, exerts a very powerful action on the animal system, but this result, as we shall show, may be explained without any hypothesis as to the presence of hydroxyl.

Cresols.

These compounds may be regarded chemically as phenol in which an atom of hydrogen is replaced by a molecule of methyl, the general formula for ortho, meta and para compounds being $C_6H_4(CH_3)OH$. As already stated all three act as sensory and motor paralysants. In the cases of the three isomers of this series, ortho, meta and para, it appears that there is a marked difference between the action of the ortho and para compound on the one hand and that of the meta compound on the other, the ortho and para compounds acting as stimulants to the inhibitory apparatus of the heart, while the meta compound has no such influence. Considered as cardiac depressants the order of intensity of action is ortho, para, meta, the last being least active. The same is true for the action on the nervous system of the frog. On the other hand metacresol acts more powerfully than the other two upon the vaso-motor system. From this it appears that in speaking of the order of intensity it will always be necessary to state the mode of action, since the order may vary with this and is, therefore, not absolute. It further appears that the replacement of an atom of hydrogen in phenol by a molecule of methyl changes the mode of action on the system, which is not the case, as we have seen, in replacements by hydroxyl, within the limits, at least, to which we have confined ourselves.

It is of importance to study these replacements from various points of view. Thus in cresol an atom of hydrogen within the phenyl molecule C_6H_5 is replaced by a molecule of methyl, CH_3. But in anisol, $C_6H_5.OCH_3$, the replacement of hydrogen by methyl takes place in the molecule of hydroxyl. Similar replacements occur in all, or nearly all, the di- and trihydroxyl derivatives of benzol. The fact that in cresols and all the higher phenols the hydroxyl OH prevents the oxidation of the alkyl group—for instance, CH_3—by chromic-acid mixture is worth noting here. Thus chromic acid does not oxidize $C_6H_4CH_3OH$. But when the hydrogen in the hydroxyl group is also replaced by an alkyl, the group which replaces hydrogen in the phenyl molecule is oxidized and ethers of the oxy-acids are formed. Thus $C_6H_4.CH_3.OCH_3$ yields $C_6H_4\begin{cases}OCH_3\\CO_2H\end{cases}$. It would therefore seem probable that the compound $C_6H_4.CH_3.OCH_3$ would act upon the system in a very different manner from the compound $C_6H_4.CH_3.OH$, or cresol, if the physiological action depends upon facility of oxidation. Materials for deciding this question are not at present available.

Since it appears at least probable that the intensity of the action of the cresols is greater than that of phenol, it becomes a question whether the successive replacement of hydrogen in phenol by an alkyl, as for instance methyl, increases toxicity. Di-, tri-, tetra- and pentamethylphenols have been obtained, but their physiological relations have not yet been studied.

Of the six possible isomerides with the general formula $C_6H_3(CH_3)(OH)_2$, four are known and will afford opportunities for determining whether replacements of an atom of hydrogen by a molecule of methyl in bodies of this class give results which are similar to those produced by replacements of hydrogen in phenol. Finally, it is very desirable to study the actions of the chlorine and bromine derivatives of the mono-, di- and trihydric phenols in which chlorine and bromine replace hydrogen. The results of such an investigation will enable us to make various important comparisons. It is also advisable to study in this connection the amido-benzols, since the physiological relations even of aniline have not been carefully examined, and we are acquainted with di-, tri-, tetra- and even pentamidobenzols.

The following tabular view will show what derivatives of phenol have been studied and also serve to indicate what substituted compounds promise to yield important results:

Phenol.	Phenol.	Phenol.	Phenol.
C_6H_5OH	C_6H_5OH	C_6H_5OH	C_6H_5OH
Dihydric phenols,	Dimethylphenol,	Triamidobenzol,	Tetrachlorphenols,
$C_6H_4(OH)_2$.	$C_6H_5(CH_3)_2OH$.	$C_6H_3(NH_2)_3$.	C_6HCl_4OH.
Trihydric phenols,	Trimethylphenol,	Tetramidobenzol,	Pentachlorphenols,
$C_6H_3(OH)_3$.	$C_6H_2(CH_3)_3OH$.	$C_6H_2(NH_2)_4$.	C_6Cl_5OH.
Tetrahydric phenols,	Tetramethylphenol,	Pentamidobenzol,	Anisol,
$C_6H_2(OH)_4$.	$C_6H(CH_3)_4OH_4$.	$C_6H(NH_2)_5$.	$C_6H_5OCH_3$.
Pentahydric phenols,	Pentamethylphenol,	Monochlorphenol,	Monomethoxyphenol,
$C_6H(OH)_5$.	$C_6(CH_3)_5OH$.	C_6H_4ClOH.	$C_6H_4OCH_3OH$.
Hexahydric phenols,	Amidobenzol,	Dichlorphenol,	Dimethoxybenzols,
$C_6(OH)_6$.	$C_6H_5NH_2$.	$C_6H_3Cl_2OH$.	$C_6H_4(OCH_3)_2$.
Cresols,	Diamidobenzol,	Trichlorphenol,	
$C_6H_4CH_3OH$.	$C_6H_4(NH_2)_2$.	$C_6H_2Cl_3OH$.	

The chinons, oxychinons and hydrochinons deserve attention in this connection.

Tables like those which we have given will be found extremely convenient in such investigations as we have undertaken. They enable us to take in at a glance the compounds whose physiological actions should be compared by placing two or more tables side by side and drawing connecting lines between corresponding terms, as for instance, trichlorphenol, $C_6H_2Cl_3OH$, and trimethylphenol, $C_6H_2(CH_3)_3OH$, etc.

Nitrophenols.

The three mononitrophenols are embraced under the general formula $C_6H_4NO_2OH$, and we have, of course, ortho, meta and para modifications. The intensity of toxic action has been shown to increase from the ortho to the para compound. The action of all three compounds is to a large degree concentrated on the circulation, and all kill by cardiac depression when injected into the jugular vein, and not by respiratory failure, and they have almost no effect on the nervous system. On the other hand the ortho and meta compounds in doses of from 0.060 to 0.075 gram to the kilo, stimulate the vagi, while the para compound depresses the vagi even in so small a dose as 0.01 gram. Ortho- and meta-nitrophenol lower temperature while para-nitrophenol raises it, for equal doses to the kilo. We seem here to have clearly defined differences between the ortho and meta compounds on the one hand, and the para compound on the other.

(Since the three mononitrophenols contain a molecule of NO_2 replacing hydrogen, we may compare their action with that of the alkaline and alkyl nitrites, bearing in mind, however, that the

chemical function is not the same in the different cases. In like manner the comparison may be made with the iso-nitrites.)

Dinitrophenol, $C_6H_3.OH.(NO_2)_2$ (1, 2, 4).

The action of this compound upon the animal system is, as we have shown, very similar to that of the mononitrophenols and may in fact be regarded as the same. On the other hand it is for equal doses per kilo more powerful. The same is true for the action of *trinitrophenol*, $C_6H_2.OH(NO_2)_3$ (1, 2, 4, 6). Comparing the last two cases with those of the mononitrophenols we find that the action, as far as can be determined, depends essentially upon the proportion of the NO_2 in the compounds, increasing in intensity with the relative quantity of the nitrogen compound.

Nitrobenzols, $C_6H_5.NO_2$ *and* *m*-$C_6H_4(NO_2)_2$.

For better comparison with the corresponding phenol compounds we may write them $C_6H_4.NO_2.H$ and $C_6H_3.(NO_2)_2.H$. The physiological actions of these two do not, as we have shown, differ essentially, except in intensity, and are apparently less powerful than those of the corresponding phenol compounds. The relatively large proportion of the NO_2 in the benzol compounds would lead us to expect a more powerful action on the part of the two nitrobenzols.

Nitranilines, $C_6H_4(NO_2)NH_2$ (*o*-, *m*- and *p*-).

These three compounds all stimulate the peripheral ends of the vagi in the heart and produce methæmoglobin or otherwise alter the hæmoglobin in the blood. The nervous effects are feeble and depend apparently upon the changes in the blood. The para compound is most active; the ortho compound comes next in order, while the meta compound is least energetic. The action of aniline is exerted mainly upon the nervous system, resembling in some respects that of ammonia, but differing particularly in the fact that true tetanus is never produced.[1] The introduction of a molecule of NO_2 completely changes the nature of the action and concentrates its action upon the circulatory system, the nervous phenomena being greatly reduced.

[1] Brunton-Croonian Lectures.

Toluidines.

These may be regarded chemically as anilines in which an atom of hydrogen in the phenyl is replaced by a molecule of methyl. They differ from methylaniline in the fact that in these last the replacement is in the NH_3 molecule. We have shown that the order of intensity of action in the case of the three toluidines is lowest with the ortho and highest with the para compound. All three break down the blood and produce methæmoglobin. All kill by failure of respiration. All lower temperatures, both normal and abnormal, and all decrease reflex activity by acting on the spinal cord.

On comparing the actions of the toluidines, it appears that while there is a distinct difference between the intensity of the actions upon the system of the ortho, meta and para compounds, there is no appreciable difference in the nature of the actions. Since toluidines are embraced under the general formula $C_6H_4CH_3NH_2$, they admit of direct comparison with aniline of which the formula is $C_6H_5NH_2$.

We note then the important fact that the replacement of an atom of hydrogen by a molecule of methyl has the general effect of diminishing the actions upon the nervous system and of increasing them upon the vascular system.

(To be continued.)

Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

X.—THE NITRITES OF SOME AMINES.

By W. A. Noyes and H. H. Ballard.

In a previous article by one of us[1] the statement is made that the nitrite of 1.4-diaminocyclohexane is decomposed on boiling its solution in water, and that the decomposition and its products would be studied. The results of this study are recorded below.

The diamine was prepared according to the directions given in an article by v. Baeyer and Noyes,[2] and by a modification of this

[1] This Journal **15**, 545. [2] Ber. d. chem. Ges. **22**, 2168.

suggested by an article of v. Baeyer's,[1] the details being furnished us privately by the author, though they have since been published.[2] As finally adopted the method consisted of the following steps: From succinic diethyl ester to succinosuccinic ester; from this by saponification with dilute sulphuric acid to 1.4-diketocyclohexane; from this by treatment with hydroxylamine to the dioxime, and finally by reduction with sodium in absolute alcohol to the diamine. The base was distilled from the alkaline solution with steam, the distillate being collected in a vessel containing hydrochloric acid. The solution thus formed was evaporated to dryness on the water-bath to remove the excess of acid. Then just enough water was added to make a hot saturated solution, to which alcohol (four or five volumes) was added and the mass allowed to cool. By this means most of the chloride was precipitated in pure condition. It was then filtered and washed with alcohol.

A determination of chlorine gave the following:

0.1127 gram gave 0.1722 gram AgCl.

	Calculated for $C_6H_{14}N_2Cl_2$.	Found.
Cl	37.97	37.88

In the reduction of the oxime it was found best to use small quantities (2–3 grams) of the substance, to boil the solution before adding sodium, and to keep enough alcohol in the flask to retain all solid matter in solution. Without this precaution a precipitate was formed which interfered with the reduction.

Decomposition of the Nitrite.—On adding sodium nitrite to a solution of 1.4-diaminocyclohexane chloride there is almost immediately an evolution of gas which at ordinary temperatures is very slow, but becomes quite marked on warming the solution, and before the temperature of boiling water is reached becomes very vigorous. At the same time there is perceived an odor which has been shown to be that of dihydrobenzene.

For the purpose of observing the rate of evolution and the amount of gas evolved, the solution to be tested, in this as well as in all other experiments described, was placed in a flask as small as could be conveniently used, and this was connected with a nitrometer. The flask was heated sometimes in a steam-bath or a vessel of boiling water and sometimes over a free flame. The

[1] Ann. Chem. (Liebig) 278, 91. [2] Ber. d. chem. Ges. 25, 1037.

latter method was found more convenient when using larger quantities, and the liquid which distilled was returned by means of a small inverted condenser.

In every instance at the end of half an hour about one-fourth of the total nitrogen had been evolved and the rate of evolution had become very slow. The curve plotted from readings made at intervals of one minute appears to be of the nature of a parabola, the ordinates representing volumes, the abscissæ time. At the end of eight hours heating usually 35–40 per cent. of the total nitrogen had been evolved.

In many experiments, especially where larger quantities were used, a portion of the diamine was recovered. In two instances careful account was taken of the various quantities, and the following figures deduced:

	I.	II.
Chloride of diamine taken,	6.45 grams.	1.00 gram.
" " recovered,	1.89	.39
Wt. of nitrogen obtained,	.70	.089
Percentage of nitrogen obtained,	10.85	8.88
Percentage of nitrogen equivalent to one atom of nitrogen in diamine chloride,	14.96	14.96
Percentage of theoretical yield,	72.5	59.4
Percentage of diamine chloride decomposed,	70.7	61.0

If in the reaction only one amine group is concerned the last two figures should be the same. The fact that small quantities of dihydrobenzene were formed in every decomposition accounts for the somewhat high percentage of nitrogen in I.

In another series of experiments a solution of the nitrite of the base was prepared by adding silver nitrite in calculated quantity to the chloride of the base in solution, and shaking the mixture for several hours. At the end of this time the solution was filtered and heated as above described. There was no apparent difference in either the rate of decomposition or the products of the reaction.

In a third series, having previously shown that the decomposition concerned principally only one amine group, the chloride of the base and sodium nitrite were mixed in the proportion of one molecule of each and heated, in which case the decomposition took place practically as it had in each of the others. The isola-

tion of the products of decomposition was accomplished in two ways, both giving the same results:

First, the liquid which had been heated was rendered strongly alkaline with caustic soda, saturated with salt and then extracted several times with ether. To the extract was added an excess of hydrochloric acid and the whole evaporated to dryness. The residue was dissolved in as little water as possible and a solution of chlorplatinic acid added, whereby was caused the almost complete precipitation of the undecomposed diamine, the chloroplatinates of the other bases present remaining in the solution, which after filtration was evaporated to dryness *in vacuo* over sulphuric acid. From the residue by crystallization from strong alcohol were obtained the chloroplatinates of the tetrahydroaniline and 1.4-aminohydroxycyclohexane. By extracting the solution after heating to decompose the nitrite and before adding the alkali, a small quantity of dihydrobenzene could always be obtained and recognized by its odor.

The second method of separation was as follows: The solution after decomposition of the nitrite was made strongly alkaline with caustic soda, and the bases thus set free distilled with steam into a receiver containing hydrochloric acid. The solution of chlorides thus obtained was evaporated to dryness on the water-bath and the residue extracted with strong alcohol, whereby an almost complete separation of the undecomposed base was effected, the chloride being left undissolved and in a practically pure condition. The alcoholic extract, evaporated to dryness, left a mixture of the chlorides of tetrahydroaniline and 1.4-aminohydroxycyclohexane, which were separated as chloroplatinates, as before. In the products of several decompositions unsuccessful efforts were made to detect the presence of chinite.[1] Dihydrobenzene was detected by its odor and the color-reaction with concentrated sulphuric acid in the presence of alcohol.[2] The amounts obtained were, however, so small that none of the other chemical properties could be identified. In one of the experiments in which a larger quantity of diamine chloride was used, the gases, before being collected for measurement, were passed through absolute alcohol cooled by ice. The solution thus obtained smelled very strongly of dihydrobenzene and gave the color very readily on the addition of sulphuric acid. By observing the liquid condensed in the inverted

[1] Ann. Chem. (Liebig) **278**, 92. [2] *Ibid.* **278**, 95.

condenser it could be seen, however, that the amount of oily matter was very small.

It seems, therefore, that in the decomposition of the nitrite of 1.4-diaminocyclohexane one amine group is principally concerned, and that the main products are salts of tetrahydroaniline and 1.4-aminohydroxycyclohexane. It will be shown later that the nitrite of the former base also decomposes on heating.

Δ³-Tetrahydroaniline Chloroplatinate. — The salt is easily soluble in water, very difficultly soluble in hot or cold absolute alcohol, easily soluble in hot alcohol containing a little water. From this solution, on cooling, scaly crystals separate, which when dry have a pale, dull yellow color, and melt with decomposition at 210°, beginning to blacken at about 205.°

Determinations of platinum resulted as follows:

I. 0.0411 gram gave 0.0132 gram Pt.

II. 0.0439 gram gave 0.01415 gram Pt.

Calculated for $(C_6H_{12}N)_2PtCl_4$.	Found.	
	I.	II.
32.28	32.12	32.23

1.4-*Aminohydroxycyclohexane Chloroplatinate.* — This substance also is soluble in water, insoluble in absolute alcohol, but quite soluble in cold, and much more easily soluble in boiling strong alcohol. When mixed with the tetrahydroaniline chloroplatinate, the two may easily be separated by crystallization from hot alcohol.

The crystals from alcoholic solution are flat, oblong plates, regular in form and often in cross-like pairs. When dry the mass has a satiny luster and a bright canary-yellow color, darker than that of the tetrahydroaniline chloroplatinate.

Determinations of platinum gave the following:

I. 0.0335 gram gave 0.0104 gram Pt.

II. 0.0960 gram gave 0.0295 gram Pt.

Calculated for $(C_6H_{10}{<}^{OH}_{NH_2})_2PtCl_4$.	Found.	
	I.	II.
30.47	31.04	30.73

All the analyses of this substance gave high results, indicating that there was a loss of water caused by heating the substance to dry it before weighing. A portion of the freshly prepared salt was therefore dried in the air and weighed. It was then heated in a xylene-bath for 20 minutes and again weighed, and this treat-

ment repeated. The loss in weight at the end of the first 20 minutes was 5.39 per cent. Calculated loss for two molecules of water is 5.64 per cent. The mass had lost its luster and darkened very slightly, showing some deeper-seated decomposition. At the end of the second twenty minutes the loss amounted to 15.58 per cent., the xylene in the bath having all evaporated and the temperature risen to 165°. The color had also become very dark. The salt was finally heated over the free flame and the amount of platinum determined, giving 30.71 per cent. based on the weight of air-dried salt.

The fact that the melting-point of the aminohydroxycyclohexane chloroplatinate is the same as that of the tetrahydroaniline salt also indicates the passage of the former to the latter on heating.

Because of lack of material no very careful study of this phenomenon was made, but it seems from the changes of color, luster and weight that take place even when the salt is only moderately heated, that there is a loss of water and formation of tetrahydroaniline chloroplatinate, and that other changes take place at the same time.

Tetrahydroaniline Nitrite.—The tetrahydroaniline formed in the decomposition of 1.4–diaminocyclohexane nitrite is in all probability the Δ^3 variety, and therefore if we accept Kekulé's formula for benzene, the double union is in the same relation to the amine group as in the β-tetrahydronaphthylamine whose nitrite is stated by Bamberger and Lodter [1] and Bamberger and Müller [2] to be perfectly stable in boiling water. It was therefore thought interesting to test the stability of the tetrahydroaniline nitrite. The chloride was prepared by passing hydrogen sulphide into water containing the chloroplatinate in suspension. The solution thus obtained was evaporated to dryness on the water-bath, and the trace of acid remaining was neutralized with a very dilute solution of caustic soda, and then an excess of sodium nitrite added and the solution heated in a bath of boiling water. The evolution of gas did not begin until the flask had remained for some time in the bath, and was very slow. In 25 minutes only one-sixth of the total nitrogen had escaped. It seems, therefore, that while the nitrite of tetrahydroaniline is not stable in boiling water, it is much more stable than the nitrite of 1.4-diaminocyclohexane.

[1] Ber. d. chem. Ges. **21**, 854. [2] *Ibid.* **21**, 1116.

β-Tetrahydronaphthylamine Nitrite (*alicyclic*).—The conduct of the nitrite of Δ^3-tetrahydroaniline rendered it desirable to test quantitatively the conduct of the nitrite of β-tetrahydronaphthylamine. To our surprise it was found to decompose on heating its solution to 100°, and its conduct in this regard is almost exactly like that of Δ^3-tetrahydroaniline under the same conditions. This result is so different from the conduct which the statement of Bamberger and Lodter[1] led us to expect that we are compelled to believe that they did not have a specimen of the pure nitrite, but that the substance with which they experimented (obtained by passing nitrous anhydride into an ethereal solution of the base) consisted chiefly of the nitrate. The analysis reported gives an amount of nitrogen which agrees much better with that required for the nitrate than for the nitrite, when it is noticed that all of the other nitrogen determinations reported in the article give high results, as is usual. Also we find that the nitrite melts with decomposition at 136°, while the nitrate, which we have prepared, melts at 215°. But a mixture of about 3 parts nitrate and one part nitrite melts at about 160° with the phenomena described by Bamberger and Lodter. We prepared the nitrite by precipitation from a strong solution of the chloride by means of a solution of sodium nitrite. The chloride melted at 242°–243°, instead of at 237° as given by Bamberger and Lodter.

The nitrite is quite soluble in water and in cold solution shows no immediate evidence of decomposition, but on being heated to the temperature of steam quite an energetic evolution of nitrogen takes place.

Using 0.2314 gram nitrite—

in the first 18 minutes 6.4 cc. gas was evolved = 21 per cent.
" " 32 " 8.2 " " = 27 "
in 174 " 14.3 " " = 47 "

so that in the course of three hours nearly 50 per cent. of the nitrite had been decomposed. A colorimetric determination of the nitrous acid in the salt used in the experiments showed the purity of the compound.

In a second experiment, to 0.1672 gram of the chloride were added 0.0005 gram of caustic soda and 0.055 gram of sodium nitrite, and the mixture heated as before in steam. There was a

[1] *Loc. cit.*

slow evolution of gas which corresponded in rate almost exactly with that of the Δ^3-tetrahydroaniline. At the end of seven and one-half hours about two-fifths of the total nitrogen had been collected.

In a third experiment sodium nitrite was added directly to a solution of the chloride and the liquid tested to be sure that it was not acid. On heating, the evolution of gas was decidedly more rapid than in the second experiment, but approximately the same as in the decomposition of the nitrite of the base alone.

It seems therefore that the nitrite of β-tetrahydronaphthylamine in water solution, either neutral or very faintly alkaline, decomposes at the temperature of steam.

2.5-*Diaminohexane Nitrite.*—To compare the relative stability of a chain compound as nearly as possible analogous to 1.4-diaminocyclohexane nitrite, 2.5-diaminohexane chloride was prepared[1] and heated in the presence of an excess of sodium nitrite to the temperature of steam, and the evolved gas collected. At the end of 5 minutes about one-third the total amount had been given off; in 15 minutes about one-half; and at the end of 11 hours an amount of nitrogen equal to 22.7 per cent. by weight of the chloride used. 22.14 per cent. is equivalent to 3 atoms of nitrogen. It appears therefore that the substance is much less stable than the corresponding ring compound, 1.4-diaminocyclohexane nitrite.

Conclusion.

The fact which gave rise to this investigation was that in the decomposition of 1.4-diaminocyclohexane nitrite only one of the four atoms of nitrogen seemed to be given off, and consequently there was a possibility of a condensation within the molecule.

This idea has been shown to be incorrect. After one-fourth of the nitrogen has been given off the decomposition becomes very slow, but continues. Furthermore, by an examination of the products, the decomposition has been shown to be normal and to concern principally one amine group, the splitting off of which and the establishing of the double union seem to render the resulting compound more stable, but at the same time not perfectly so.

The similarity in the behavior of the nitrites of Δ^3-tetrahydroaniline and β-tetrahydronaphthylamine is a slight indication that

[1] Ber. d. chem. Ges. **23**, 168, 2100.

the two compounds have a similar structure. We do not attach much importance to analogies of this kind, and especially we do not consider that any valuable conclusion as to the structure of benzene can be drawn from them. In any case, however, the analogies do not favor the centric formula for benzene. With that formula there is no double union in β-tetrahydronaphthylamine where its analogy with the Δ^3-tetrahydroaniline would lead us to expect one.

April 25, 1894.

A STUDY OF THE CONSTITUENTS OF THE NODES AND INTERNODES OF THE SUGAR CANE.

By J. L. Beeson.

It is a belief among sugar-planters that the nodes of the cane stalk (the joints) are the main source of the reducing sugars contained in the expressed juice. In order to throw light upon this and other questions, a study was made this season of the constituents of the nodes and internodes of the cane as follows: Twenty stalks were selected from the field, of as near the same size and number of joints as possible. The nodes were separated from that portion lying between the nodes—the internodes—with a fine saw. These separate portions were each passed twice through hand-roller mills, an effort being made to give as nearly as possible the same pressure and relative extraction of juice from the nodes as the internodes. The two juices thus obtained were markedly different in appearance and constituents. That from the nodes was in every case highly colored, gave a heavy precipitate with a solution of subacetate of lead, and a heavy coagulum on heating to the boiling-point of the juice; while that from the internodes was clear, light in color, gave only a small precipitate with subacetate of lead solution, and no appreciable coagulum on heating. This difference in coagulable bodies indicates a wide difference in the water-soluble albuminoids in the two juices. In the two following tables are given the analyses of the juices:

Analysis I.— Twenty stalks, purple variety, plant cane. Average weight of stalk, 3 pounds.

		Total Solids.	Reducing Sugars.	Sucrose.	Solids not Sugars.
Tops	Nodes	15.5	0.66	12.7	2.64
	Internodes	16.8	1.20	15.0	1.60
Middles	Nodes	16.2	0.20	13.5	2.90
	Internodes	17.6	1.00	15.6	1.00
Butts	Nodes	14.2	0.26	11.9	2.04
	Internodes	17.2	0.89	15.1	1.21

Analysis II.— Twenty stalks, purple variety. Average weight of stalk, 3 pounds.

		Total Solids.	Reducing Sugars.	Sucrose.	Solids not Sugars.	Fiber.
Tops	Nodes	15.3	0.18	11.3	3.82	15.6
	Internodes	16 9	1.25	14.3	1.35	8.6
Middles	Nodes	16.7	0.07	13.7	3 07	15.9
	Internodes	17.7	0.98	16.0	0.72	8 0
Butts	Nodes	15.7	0.15	12.8	2.75	18.2
	Internodes	17.7	0.61	16.4	0.69	8.1

It will be seen that there was found more glucose or reducing sugars in the tops of the stalk than in the butts. This is to be expected, since the tops are less mature. Also that there is approximately twice the percentage of fiber (that portion of the stalk which is insoluble in water) in the nodes as in the contiguous internodes, the butt nodes showing the highest percentage. But the most striking fact is the marked decrease in reducing sugars and a like increase in solids not sugars (which are mainly albuminoids, gums and mucilages) in the nodes over that of the contiguous internodes. This wide difference in content of reducing sugars in the different portions of the stalk is surprising, in view of the readily diffusible nature of these bodies. The cane from which the samples were taken had been blown down, and it was noticed that the eyes had very slightly sprouted, yet their rootlets had not taken hold in the soil. It was thought possible therefore that this low percentage of reducing sugars in the node or joint was due to this fact: that the incipient growth of the eye was at the expense of the glucose in that region, using it up more rapidly than it could diffuse from the adjoining internode—the internode containing the bulk of the juice. This hypothesis, of course, assumes glucose—and not starch, as is maintained by Sachs and others—to be the first visible product of plant-assimilation. Since

pure starch is nowhere found in the cane,[1] it is difficult to see how this body could in this case be a product of plant-assimilation. It would appear more reasonable that a sugar, in the case of cane, supplies the food for the first stages of growth.

If the above hypothesis be correct, namely, that the decrease in reducing sugars in the node is due to the incipient growth of the eye, then canes bearing normal eyes should not show this difference, and, on the other hand, canes bearing sprouts, yet whose rootlets had not taken hold in the soil, should show a difference in content of reducing sugars similar to that in cases I and II, with a *lower percentage* in the internode, unless some of the sucrose should be inverted by the growing sprouts as a further supply of glucose for food. In order to throw light on this point the following analyses were made: (1) of canes having normal eyes, (2) of canes having large or slightly sprouted eyes, (3) of canes bearing sprouts.

Analysis III. Normal eyes, 4 stalks, striped variety, plant cane. Average weight of stalk, 3 pounds.

	Reducing Sugars.	Sucrose.
Nodes of whole stalk	0.40	12.0
Internodes of whole stalk	1.23	15.5

Analysis IV. Large eyes—sample and weight same as in above.

	Reducing Sugars.	Sucrose.
Nodes of whole stalk	0.50	12.8
Internodes of whole stalk	1.11	13.4

Analysis V. Sprouted eyes.—Same variety as in above. Upper halves and upper thirds from 4 stalks, sprouts from two to six inches long.

	Reducing Sugars.	Sucrose.
Nodes of upper halves and thirds	0.3	12.00
Internodes of upper halves and thirds	0.9	16.00

These canes were selected from the same plat, of as near the same size and number of joints as possible, were analyzed the same afternoon, and as soon as possible after expressing the juice. From analysis III it will be observed that canes having normal eyes show the same wide difference in content of reducing sugars in the nodes and internodes, and this difference cannot be due in the main to the incipient growth of the eye. Analysis of another

[1] Bull. 10, 1st Ser., p. 320, La. Sug. Expt. Sta.

variety of cane having normal eyes confirmed the results of analysis III.

Upon comparing analysis V with analyses III and IV it will be seen that in the canes bearing sprouts (yet whose rootlets had not taken hold in the soil) there is found less glucose in both the nodes and internodes than in the case of canes having normal, and larger eyes. This difference is augmented when it is remembered that in case V the content of reducing sugars in the upper halves and upper thirds of the stalk—which are richer in reducing sugars—is compared against that of the whole stalk in cases III and IV. It would therefore appear that the growth of the sprouts on the stalk was at the expense of the glucose or reducing sugars, and that, in the case of the cane, glucose is the first visible product of plant-assimilation. During germination it is likely that the initial growth is at the expense of the ready formed glucose in the stalk—and the ripest canes have been shown to contain this sugar—and that the sucrose is attacked and inverted as a future supply of food when it is needed by the young plant. If so, it may be that there is permitted by the young plant a certain using up of this ready-formed glucose, a certain glucose minimum, before the sucrose is attacked as a further supply of food. Then by working with canes bearing longer and longer sprouts, the rootlets of which had not taken hold of the soil, it was hoped that this glucose minimum might be established for the sugar cane; but an untimely frost killed the cane and thus cut short the work.

Since the canes having normal eyes showed this marked decrease in content of reducing sugars in the nodes over that in the internodes, and since these bodies are so readily diffusible, it was thought most likely (1) that there were some physiological forces at work in the plant organism connected with the ripening of the cane which were using up the reducing sugars more rapidly in the node than they could diffuse in from the adjoining internode; (2) that the decrease in reducing sugars and increase in "solids not sugars" in the node mutually account for each other; (3) that as the cane ripens these simpler sugars are passing by the condensation of the molecules into more complex and less soluble forms—*e. g.* into gums and mucilages—and that the amides and glucoses are uniting in the presence of sulphur compounds to build up albuminoid bodies more rapidly in the region of the vital organs of the plant—the node—as a store of food for the young plant before it

has taken sufficient hold of the earth to draw sustenance from the soil and atmosphere. Then the function of the node would be similar to that of the seeds in the case of flowering plants, with the sucrose of the internode as a further food reserve.

If the above explanation and hypothesis be correct we should expect to find in the juice expressed from the nodes of growing canes fairly matured, a decrease in reducing sugars, an increase in soluble carbohydrates not sugars, and an increase in albuminoids. Remembering that the two latter classes of bodies constitute the bulk of the "solids not sugars," by reference to analyses I and II it will be seen that this was found to be true, and by analysis of the fiber (that portion of the cane which is insoluble in water) we should expect to find in the nodes an increased quantity of water-*insoluble* albuminoids, of the celluloses, and of those *insoluble* carbohydrates not sugars which lie in their constitution intermediate between the celluloses on the one hand and the *soluble* carbohydrates not sugars on the other. By the action of ferments during germination the soluble and insoluble albuminoids would yield amides and glucoses, and the soluble and insoluble carbohydrates not sugars would yield reducing sugars—all of which as food for the young plant. The insoluble bodies above mentioned, the celluloses and ash, constitute the "fiber" in analysis II, which it will be seen has approximately twice the percentage in the nodes as in the internodes. The fiber of the nodes and internodes from the samples in analysis II was thoroughly extracted with first cold and then hot water to remove all soluble nitrogenous bodies, and the albuminoids estimated by determining the total nitrogen in the fiber by Kjeldahl's method, and multiplying by the factor 6.25, and found to be: in the nodes, 1.9 per cent.; in the internodes, 1.6 per cent., showing an excess in the nodes.

For the estimation of the insoluble carbohydrates not sugars in the nodes and internodes, the fiber (same as in preceding analysis) was extracted with cold and hot water until only a trace of soluble carbohydrates was revealed in the washings by the α-napthol test, then boiled for one hour with a 1-per cent. solution of sulphuric acid and filtered. The sulphuric acid was removed by means of barium carbonate, and the reducing sugars thus formed, as estimated by means of Fehling's solution, were as follows: In the nodes, 13 per cent.; in the internodes, 8.8 per cent. These and the preceding estimations were made in duplicate, the duplicates agreeing closely.

It will be remembered that there was obtained in every case a heavy coagulum by heating the juice from nodes, while practically none was gotten from boiling that from the internodes. This indicates a large excess of albuminoids in the juice of the nodes. Just here it was highly desirable to have determined quantitatively the percentage of albuminoids and non-albuminoids or amides in these two juices, but it could not be done on account of the accumulation of work during the sugar season.

Vegetable physiologists teach us that when seeds germinate, or when the plant organism suffers decay, the chemical processes taking place are the reverse of those during the process of ripening: namely, that the more complex and less soluble forms pass by the action of ferments into simpler and more soluble ones—the albuminoids into amides and glucoses, the gums into reducing sugars, and so on. Then, if our hypothesis be correct—if the node is a storing-place of food for the young plant—we should expect to find, as the cane deteriorates, not only an increase in the total reducing sugars coming from the inversion of the sucrose (as is well known to be the case), but also an increased quantity in the node over that of the internode coming from the increased quantities of "solids not sugars" found in the juice of the node. In order to throw light upon this point three classes of canes were selected and analyzed: (a) canes cut down before the frost, and which had lain for over a month covered with leaves; (b) the soundest canes standing which also had been killed about a month previously by the frost; (c) canes standing which appeared to have suffered most, and which also had been killed by the frost. Canes which were germinating in the soil could not be used for this test, for, it has been evinced, the growth of the young plant would probably have been at the expense of the reducing sugars. Four stalks of each class were analyzed with the following results:

	Samples from same plat as in Analysis I.	Total Solids by Bux hydrometer.	Reducing Sugars.	Sucrose.	Solids not Sugars.
Class A	Whole of nodes,	14.91	0.79	10.5	3.57
	" " internodes,	15.40	1.25	10.8	3.30
Class B	Whole of nodes,	12.77	0.95	9.1	2.74
	" " internodes,	14.87	1.06	12.2	1.41
Class C	Whole of nodes,	13.62	1.44	8.1	3.08
	" " internodes,	15.17	1.00	12.0	2.19

It will be seen that in the three stages of deterioration of the cane there is a gradual increase in the content of reducing sugars

in the juice of the node over that of the internode until they are in large excess of the latter. This is the reverse of what was found to be true in the case of ripening cane, analyses I and II showing an average of 0.14 per cent. of reducing sugars in the node and 1 per cent. in the internode, or a ratio of about 1 to 7. In these cases it is strange that the glucose, which is so readily diffusible, had not distributed itself equally throughout the whole stalk. But it is probable that the death of the cane brought about a change in the cell walls which prevented diffusion. Nothing short of experiments on the diffusion of glucose in dead cane can answer definitely this question. No such experiments were made.

By comparing these results with those (analysis I) of the same variety made just before the frost, it will be seen that there is an increase in the quantities of "solids not sugars" in the juice of both the nodes and internodes, that of the former here, also, being in excess. At first sight it would appear that, since the "solids not sugars" of the juice would most easily yield reducing sugars by the action of ferments during decay, there should be found a decrease in "solids not sugars" in the juice of the node corresponding to the increase in the reducing sugars. But it will be remembered that there was found in the "fiber" of the node 13 per cent. of insoluble bodies not sugars which, by the action of ferments, would most likely yield first *soluble* bodies not sugars before passing into reducing sugars. This process would increase the "solids not sugars" in the juices of both the nodes and internodes, as was found to be the case.

Further, if this explanation be correct, this process would be at the expense of what is estimated as "fiber" in the cane, and canes which had deteriorated should not only show an increase in "solids not sugars" and in reducing sugars, as was found to be the case, but also a decrease in "fiber"—that portion of the cane which is insoluble in water. As a result of several years of experimentation at this station this has been found to be the case.[1]

To recapitulate: it has been found in the course of this investigation that the juice of the nodes of the cane is quite different from that of the internodes, containing markedly less reducing sugars, more "solids not sugars," and more coagulable bodies; that the "fiber" of the nodes contains more albuminoids, more

[1] Bull. shortly to be published.

insoluble carbohydrates not sugars which readily pass into reducing sugars; that as the cane deteriorates reducing sugars are formed more rapidly in the nodes than in the internodes; and that probably glucose is the first visible product of plant-assimilation by the young cane. In our opinion these facts can be best explained by the hypothesis previously stated, namely, that the physiological function of the node in the cane is similar to that of the seeds in the case of flowering plants—to store food in the region of the eye for the use of the young plant before it has taken sufficient hold of the earth to draw sustenance from the atmosphere and soil. This hypothesis is further confirmed by the fact that the isolated nodes of the cane when planted will germinate and grow to maturity.[1]

If this be true in regard to the cane, it may be true also in the case of all varieties of plants which propagate from the nodes or joints.

LOUISIANA SUGAR SCHOOL AND EXPERIMENT STATION.

NOTES OF WORK FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA.

NO. XIX.

Communicated by F. P. DUNNINGTON.

160.—ON THE SOLUBILITY OF CREAM OF TARTAR IN ALCOHOL OF VARIOUS STRENGTHS AND AT VARIOUS TEMPERATURES.

BY J. A. ROELOFSEN.

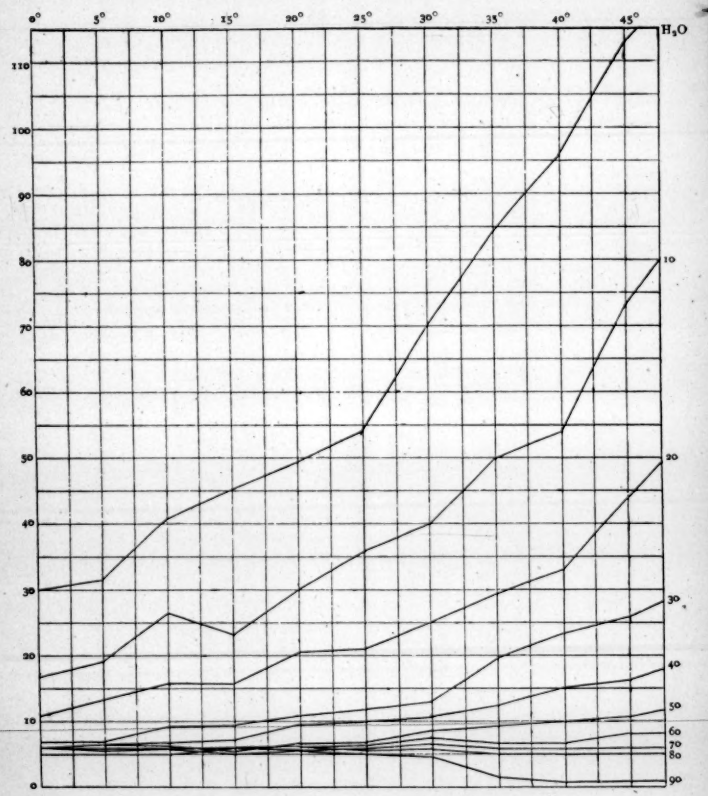
In 1891 some work was done by Mr. W. H. Wenger in this laboratory on the solubility of cream of tartar in alcohol of various strengths at about 25° C., and the result was published in this Journal.[2] With a view to enlarge the knowledge upon the subject and to ascertain the solubility at various temperatures, the following work was undertaken.

[1] Bull. 7, 1st Series, La. Sug. Expt. Sta. [2] 14, 624.

Alcohol of 93 per cent. by weight was mixed with various amounts of a saturated solution of cream of tartar, previously purified, to make liquids of different strengths. Lots containing 90, 80, 70, 60, 50, 40, 30, 20, 10, and 0 per cent. of alcohol respectively were made, and small bottles holding about 125 cc. filled with them. These were tightly corked and exposed for a number of hours, in no case less than six, to the following temperatures: 0°, 5°, 10°, 15°, 20°, 25°, 30°, 35°, 40°, 45°, 50° C. The bottles were frequently shaken. It was found necessary in the case of the weaker alcohols at the higher temperatures, and with water at all temperatures, to add some cream of tartar so as to maintain an excess and prevent supersaturation; for, except in the stronger alcohols, it was found that the amount thrown down from solution on addition of the alcohol was not sufficient to saturate the liquids at the higher temperatures.

For each determination 50 cc. were used, and this amount was drawn up into a pipette to the lower end of which was attached by means of rubber tubing a piece of glass tube 10 cm. long and 6 mm. in diameter, tightly packed with cotton-wool. In this way undissolved particles were kept from being drawn up. In a few cases it was very difficult to obtain perfectly clear solutions. The bottles subjected to the higher temperatures were packed in cotton after being taken from the hot-air chamber, to prevent loss of heat by radiation during the taking of samples, and observation of the temperature of the remainder of the liquid after the samples were taken showed no appreciable loss of heat. The samples were put into beakers, diluted with water, and determinations of the cream of tartar present made with decinormal solution of sodium hydrate, phenolphthalein being employed as an indicator. The sodium-hydrate solution was freed from carbonic acid by barium hydrate, and preserved in a bottle provided with a rubber stopper through which passed a syphon to draw off the solution as needed, and a U-tube containing solid potassium hydrate through which air was admitted. The solution was standardized against normal sulphuric acid, and this was repeated several times during the course of the work, which extended over some weeks.

Four determinations of the dissolved cream of tartar were made in each case, and wherever these results gave a considerable deviation from a regular curve more than these were made. The averages of these are given in the table, and the diagram indicates



SOLUBILITY OF CREAM OF TARTAR IN ALCOHOL.

Abscissæ represent temperatures; ordinates, milligrams dissolved in 10 cc. liquid. Figures on right of drawing represent percentage strength of alcohol.

by a separate line for water and for each strength of alcohol employed, the weight in milligrams of cream of tartar dissolved in 10 cc. as determined for each 5° of temperature from 0° to 50° C.

Milligrams of cream of tartar dissolved in 10 *cc.*

Temp.	Alcohol of percentage									Water.
	90	80	70	60	50	40	30	20	10	
0°	6.2	6.4	4.9	6.0	6.0	6.2	7.0	10.8	17.3	30.1
5°	5.5	6.0	5.1	6.0	6.8	6.8	7.1	13.2	18.8	32.0
10°	6.2	6.2	5.1	5.8	6.4	7.0	8.6	16.0	27.0	41.1
15°	5.3	6.2	6.2	6.2	5.5	7.7	8.8	15.8	23.9	44.3
20°	6.4	6.4	6.2	6.4	7.0	9.6	11.3	17.1	29.3	49.0
25°	4.7	5.5	6.0	6.8	7.0	10.3	11.7	21.4	36.4	54.1
30°	4.7	6.0	6.8	7.5	8.5	11.0	13.1	24.8	39.9	69.2
35°	1.9	5.1	5.9	6.8	9.0	12.4	18.8	28.7	49.3	83.8
40°	1.7	5.3	5.8	7.0	10.2	14.9	23.1	37.7	53.6	95.9
45°	1.7	5.3	6.0	7.9	10.7	16.5	25.8	44.2	72.6	112.8
50°	1.5	5.1	6.0	8.1	12.8	19.0	29.7	53.6	87.2	124.8

161.—THE IODINE-ABSORPTION OF SOME OF THE RARER FATTY OILS.

By J. A. Roelofsen.

The following figures on the iodine-absorption of some fatty oils were obtained according to the directions given in Allen's Commercial Organic Analysis where the process of Baron Hübl is fully described. The time allowed for the absorption was two hours in each instance. The oils came from thoroughly reliable sources; those marked * were obtained from exhibitors at the Philadelphia Centennial Exposition, and those marked † were gotten from and personally extracted by Baboo Kanny Loll Dey, Professor of Chemistry at the Medical College, Calcutta, and honorary and corresponding member of the Pharmaceutical Society of Great Britain. The oils were kept in securely stoppered bottles in a protected place. Upon opening, all, with the exception of one, which is especially noticed in the following list, were found to be in good condition. A few of the more common oils, the absorption-figures of which were already well known, and also some few of which but a single figure was found on record, were worked for the sake of comparison, but the absorption-figures of most of the oils have, as far as I have been able to ascertain, never before been determined.

Name, Commercial and Native.	Natural Source.		Iodine Absorpt.	Color.	Consistency.
†Mustard-seed oil, Sursou-ka-tel	*Sinapis nigra.*	India.	88.5	Yellow.	Liquid.
†Koosum oil	*Carthamus tinctorius.*	Lucknow, Oude.	34.	Dark yellow.	Honey-like.
Olive oil			80.9	Yellow.	Liquid.
*Grape-seed oil	*Vitis* (spec. ?)	Italy.	135.7	Yellow.	"
†Ground-nut oil, China-badam-ka-tel	*Arachis hypogaea.*	Bengal.	97.	Light yellow.	"
†Bassia butter, Mowha-ka-tel	*Bassia latifolia.*	Bengal.	61.3	White.	Buttery.
†Chaulmoogra oil	*Gynocardia odorata.*	India.	76.2	Brown.	"
†Cocoanut oil, Narcole	*Cocos nucifera.*	Ceylon.	8.3	White.	"
†Refined oil from seeds of	*Cerbera Theveta.*	India.	68.3	Colorless.	Liquid.
Vegetable wax (but slightly soluble in chloroform)		Brazil.	18.8	White.	Solid.
*Vegetable wax		Japan.	4.5	"	"
*Oleo de Badiputa	*Gomphia parvifolia.*	Brazil.	60.1	Green.	Buttery.
*Tea-seed oil	*Camelia* (spec.?)	Chin-ki-ang, China.	94.6	Yellow.	Liquid.
*Tea-seed oil	*Camelia* (spec.?)	Hangkow, China.	116.3	Light yellow.	"
*Linga oil	*Sesamum indicum.*	Philippine Islands.	101.6	Yellow.	"
*Lumban oil	*Aleurites triboba.*	"	111.8	Yellow.	"
*Babuy oil	*Eriodendron anfractuorum.*	"	93.1	Light yellow.	"
*Tuba oil	*Jatropha cureas.*	"	96.8	Light yellow.	"
*Oolæhong oil, subst. for cod-liver oil, from whole body of fish 5 inches long		British Columbia.	81.5	Light yellow.	"
*Palo Maria oil	*Calophullum inophyllum.*	Philippine Islands.	89.5	Green.	Buttery.
*Oil of Burity	*Mauritia flexuosa.*	Brazil.	46.2	Dark yellow.	"
†Fennel-seed oil, Kalazira-ka-tel	*Nigella sativa.*	Bengal.	119.2	Brown.	"
Sunflower-seed oil	*Helianthus perennis.*	India.	52.7	Yellow.	Liquid.
†Radish-seed oil, Moola-ka-tel	*Raphanus sativus.*	India.	121.	"	"
†Oil of	*Pinus deodora.*	India.	127.8	Dark brown.	"
†Almond oil (Indian)	*Terminalia cattapa.*	India.	63.6	Yellowish-white.	Buttery.
*Oleo de Andiroba	*Carapa guyanensis.*	Brazil.	60.9	"	"
*Oleo de Babosa	*Aloes brasiliensis.*	"	78.7	Yellow.	Liquid.

Name, Commercial and Native.	Natural Source.		Iodine Absorpt.	Color.	Consistency.
*Oleo de Patana	*Penocarpus* (spec. ?)	Brazil.	76.9	Yellow.	Liquid.
*Oleo da Semente de Laranja		"	95.5	Dark yellow.	"
*Oil of	*Bertholettia excelsa.*	"	93.2	Colorless.	"
*Oil of Tucum	*Bactris Tucuman.*	"	53.1	Red.	"
Lanoline		Germany.	10.9	Pale yellow.	Soft solid.
Cotton-seed oil	*Gossypium herbaceum.*	U. S.	108.7	Yellow.	Liquid.
Maize oil	*Zea Mays.*	Holland.	124.4	"	"
Chinese bean oil			138.8	"	"
†Gurjun-tel	*Dipterocarpus laevis.*	India.	171.4	Dark green.	"
*Macassar oil	*Schleichera trijuga.*	Dutch East India.	69.1	Light brown.	"
†Nim-ka-tel	*Azadirachta Indica.*	India.	64.5	Yellow.	Buttery.
†Cashew-nut oil, Hidglee-badam-ka-tel. (This was found partly decomposed.)	*Anacardium occidentale.*	India.	165.3	Dark brown.	Liquid.
†Marking-nut oil, Bhala-ka-tel	*Semecarpus anacardium.*	India.	80.	Dark brown.	"
*Ye-no-abura (oil used in prep. paper leather)		Japan.	165.4	Yellow.	"
†Linseed oil, Tesee mushina	*Linum usitatissimum.*	Bengal.	154.1	Dark yellow.	"
†Teel oil (Gingaly oil)	*Sesamum orientale.*	Bengal.	103.1	Dark yellow.	"
Seal oil			116.3	Yellow.	"
Shark-liver oil		Japan.	209.	Light yellow.	"
Mutton-bird oil		Tasmania.	112.	Yellowish-red.	"
*Turtle oil	*Peltocephalus Tracaya.*	Venezuela.	48.6	White.	Buttery.
*Blackfish oil			112.	Yellow.	Liquid.

REVIEWS AND REPORTS.

Recent Progress in Physical Chemistry.

Die Dichten gesättigter Dämpfe und ihre Beziehung zu den Gesetzen der Erstarrung und Verdampfung der Lösungsmittel. F. M. Raoult: *Ztschr. phys. Chem.* **13**, 187 (1894).—Van't Hoff's thermodynamical theory of the vapor-pressures of solutions is essentially a calculation of the change of free energy[1] accompanying the separation of solvent from the solution. When n g-mols. of non-volatile substance are dissolved in N g-mols. of solvent, a separation, by isothermal vaporization and subsequent condensation, of that amount N/n g-mols. of solvent in which one g-mol. is dissolved, requires the work (change of free energy)

$$\frac{N}{n}\int_{f'}^{f} v\,df = \frac{N}{n} RT \log \frac{f}{f'};$$

when the density d of the vapor is the theoretical. In this formula v and T are the molecular volume and absolute temperature of the vapor, f and f' are the vapor-pressures of solvent and solution, R is the "gas-constant." When the vapor-density has an abnormal value Δ (as is the case with the fatty acids), the change of free energy is

$$\frac{d}{\Delta} \cdot \frac{N}{n} RT \log \frac{f}{f'};$$

and since the same quantity, when the separation is effected osmotically by a semi-permeable membrane, is RT, we have as the most general result,

$$\log \frac{f}{f'} = \frac{\Delta}{d} \cdot \frac{n}{N}.$$

Raoult points out that for most solvents Δ/d is nearly unity, yet the variation therefrom may be appreciable. A most satisfactory confirmation of the theory is furnished by the following agreement between the Δ/d values calculated by Raoult from the vapor-pressures and those directly observed by (chiefly) Battelli, and Ramsay and Young:

Solvent.	Temperature.	Δ/d (theory).	Δ/d (observed).
Water	100° C.	1.02	1.03
Ethyl alcohol	78	1.01	1.02
Ethyl ether	20	1.04	1.04
Carbon disulphide	24	0.99	1.01
Benzene	80	1.01	1.02
Acetic acid	118	1.63	1.64

[1] See This Journal **15**, 675.

The author appends a discussion of the relation between the vapor-pressure law of dilute solutions and the corresponding laws governing their freezing- and boiling-points.

Ueber die Wärmeausdehnung und Kompressibilität von Lösungen. G. Tammann: Ztschr. phys. Chem. **13**, 174.—The thermodynamical surface of a solution is defined as that geometrical surface which represents in a system of Cartesian co-ordinates the volume of a solution as a function of its temperature and pressure. Tammann claims that the thermodynamical surface of an aqueous solution may be made to coincide very closely with that of its solvent, by a mere displacement along the pressure-axis, the equation of the surface changing from

$$v = f(p, T) \quad \text{to} \quad v = f(p - \Delta p, T).$$

He seeks to refer the slight discrepancy between this rule and the observed facts to a varying dependence of the increment Δp upon the pressure and temperature for different solutions. The paper is marred by kinetic considerations which lead nowhere.

Ueber die kontinuierliche Elektrizitätsleitung durch Gase. F. Braun: Ztschr. phys. Chem. **13**, 155.—In a series of experiments similar to those of Hemptinne,[1] the well-known Tübingen physicist has investigated the electrical conductivity of heated gases. He finds that mixtures of nitric oxide and air, and of hydrogen and chlorine, in the moment of combination, show no trace of conductivity between platinum electrodes, even when potential differences of four thousand volts are employed; that in the moment of explosion carbon monoxide and oxygen do exhibit an appreciable conductivity; and that currents of the dissociating vapors of iodine, cadmium iodide and ammonium chloride passing through tubes at temperatures ranging from 1000°–1200° C. do actually conduct, the ammonium chloride notably, while others such as carbon dioxide and steam do not show any conductivity at all. The hot gases from a spirit-lamp were observed to conduct readily between platinum electrodes, the process being arrested by the interposition of a wire gauze between the electrodes and the flame. The experiments were essentially of a qualitative nature.

Studien über Dampfspannkraftsmessungen. G. W. A. Kahlbaum: Ztschr. phys. Chem. **13**, 14.—This paper is a digest of the numerical results of a very careful and extended investigation,[2] undertaken for the purpose of establishing thoroughly trustworthy data for the vapor-pressure curves of various fatty acids, and to determine finally whether or not the dynamical and statical methods of measuring vapor-pressures yield identical results.

[1] Ztschr. phys. Chem. **12**, 244.
[2] Published under the same title in book form (Basel, 1893).

The latter question is answered emphatically in the affirmative, for Kahlbaum finds the vapor-pressures of water and of mercury, by employment of the dynamical method, to be as good as identical with those obtained by Regnault and Hertz by the statical one. A repetition, further, of Landolt's determinations with the fatty acids resulted in a correction of Landolt's figures, of sufficient amount to establish a satisfactory agreement here also between the results of the two methods. It is thus at last demonstrated that the easily executed dynamical method has every advantage over the statical one. The paper is concluded by a tabulation of the data obtained in the study of thirteen fatty acids and of various mixtures.

Primäre oder secundäre elektrolytische Wasserzersetzung. M. LeBlanc: Ztschr. phys. Chem. **13**, 163.—In the present article LeBlanc upholds against Arrhenius the view developed by himself in recent papers upon the electromotive forces of polarization, that in the electrolysis of those aqueous solutions from which hydrogen and oxygen are evolved by the current the water present suffers a primary decomposition.

To precipitate an ion upon an electrode requires an electromotive force sufficient to overbalance the counter electrolytic solution-pressure of the precipitated substance, *i. e.* its tendency to go into solution again as an ion. This solution-pressure varies from substance to substance in the same way that the vapor-pressure varies, and with low impressed electromotive forces the substances with smallest solution-pressures must necessarily be the first to be thrown out. In all aqueous solutions the hydrogen cation of water is present—in very slight concentrations, it is true, but yet appreciably present—and since the electrolytic solution-pressure of hydrogen is relatively low, this substance is usually the first to be precipitated. (The metals with still lower solution-pressures are copper, mercury and silver.) Although the current is carried through the solution in great part by the ions of the dissolved electrolytes, the concentrations of these ions being relatively great, yet the precipitation of material upon the electrodes is another thing, and involves first those substances which go out the most easily—involves for most electrolytic solutions the hydrogen and hydroxyl ions of the solvent. And as fast as these are thrown out at the respective electrodes their places are supplied by the continued (electrolytic) dissociation necessary to maintain their equilibrium-concentrations there. The decomposition of the liberated hydroxyl into water and free oxygen is of course a purely secondary reaction. When the current-density is so increased that more current passes than these ions can carry, the electromotive force immediately rises to a point at which one or more of the dissolved ions present are precipitated also.

The older hypothesis of a primary separation of all the cations at the cathode, and similarly for the anode, would require, to

account for the behavior of a solution of potassium, zinc, copper and silver salts, the complex and somewhat ridiculous assumption that secondarily the liberated potassium replaces the zinc, hydrogen, copper and silver, the zinc then replacing the last three, the hydrogen the remaining two, and the copper finally the less "positive" silver, which is thereupon deposited. It is much simpler to regard the current as carried by all the ions present, and the successive separation of the cations to follow the order of their respective electrolytic solution-pressures—as is actually observed. From this point of view it is apparent that the quantitative separation of ions from one another by electrolysis depends more essentially upon the electromotive forces employed than upon the amount of current—an entirely new development.

LeBlanc was led to this view of the primary separation of the least positive ion, by the identical values of the electromotive forces required to electrolyze a large number of aqueous acids and bases studied by him. The idea is a distinct advance in the theory of electrolysis, and the paper in question is a clear and dignified exposition of it.

Beiträge zur Stöchiometrie der Ionenbeweglichkeit. G. Bredig: Ztschr. phys. Chem. **13**, 191.—The investigation published under the above title is an unusually exhaustive and careful piece of work. The author has determined, with the employment of a high degree of experimental skill, the maximum electrical conductivities of a hundred and fifty salts in aqueous solution at 25°, and from these and older data has calculated the migration-velocities of some three hundred ions. An ingenious detail of the work is the successful measurement of the conductivities of salts of weak organic bases, after repressing their hydrolytic dissociation by the addition of an excess of the free base: an especially interesting application of the law of mass-action (or reaction-isotherm).

The author points out that the migration-velocity of the elementary ions is a pronounced periodic function of their atomic weights. In connection with many interesting facts concerning the relative velocities of complex ions, he brings forward the unexpected result that the migration-velocity of a metameric cation is the greater the more symmetrical its substitutions. He proves further that purely isomeric cations migrate at equal rates, and that in all cases the velocity decreases asymptotically with increasing complexity of structure. The paper is an important contribution to our knowledge of the ion-velocities.

Ueber die Affinitätsgrössen der Basen. G. Bredig: Ztschr. phys. Chem. **13**, 289.—With the aid of the migration-velocities of the organic cations obtained in the preceding paper, the author has determined the dissociation-constants (affinity-constants) of over forty amines and ammonium bases, finding the dissociation-equilibrium to be accurately represented in all accessible cases by the

theoretical isotherm employed by Ostwald for the acids. The quaternary bases are as strong as the fixed alkalies, the secondary bases are notably weaker (of 30–40 per cent. dissociation in $\frac{1}{250}$-normal solutions), the tertiary and primary amines are the weakest of all. Ammonium hydroxide is but slightly stronger than acetic acid; the substituted phosphonium, arsonium, stibonium, sulphinium and tellurinium bases are very strong; the tin and mercury bases very weak. The author demonstrates that measurement of the electrical conductivity of the hydrochlorides of very weak bases yields data from which the affinity-constants of the free bases can be found with the aid of the law of mass-action, and he concludes the paper by pointing out various errors and misapprehensions into which Lellmann and his pupils have fallen in their recent attacks upon the ion-theory of electrolytic solutions.

Ueber die Zersetzung des Jodwasserstoffgases in der Hitze. Max Bodenstein: Ztschr. phys. Chem. **13**, 56.—The material for this exhaustive study of the dissociation of hydriodic acid was prepared synthetically by conducting iodine-vapor and hydrogen over hot, platinized asbestos, and absorbing by water the acid produced. It could then be obtained when desired by heating this solution and purifying the evolved gas (from water) by phosphorus pentoxide and (from iodine) by a pure red phosphorus. The yield was about 90 per cent. of the iodine employed. The usual statement that dissociation begins near 180° was shown to be incorrect, for an appreciable although slow decomposition takes place at 100°. At 448°, the temperature of boiling sulphur, the dissociation according to the equation

$$2HI \gtrless H_2 + I_2$$

amounted to 21.5 per cent. of the gas used, and the amount remaining uncombined in the formation of the acid from free hydrogen and iodine was 21.0 per cent., so that the dissociating system was beyond question in a true state of thermodynamical equilibrium. The degree of dissociation in vessels filled under atmospheric pressure changed from 16.4 per cent. at 290° to 23.6 per cent. at 518°, passing through a minimum near 325°. The rise from this point proves that the heat of formation at all higher temperatures is positive; it must accordingly be negative (heat absorbed) at lower temperatures, which is in accordance with the thermochemical determinations of Thomsen.

The velocities with which the dissociation- and formation-reactions occur were unexpectedly found to be entirely regular; the progress of the dissociation was accurately represented by the integrated form of the differential equation

$$\frac{dx}{dt} = C(1-x)^2 - C'\left(\frac{x}{2}\right)^2,$$

representing the velocities of bimolecular reactions; C and C' are constants, the dissociation is x per cent. at the time t. This is the first case in which a uniform reaction-velocity has been observed in gaseous systems. The velocity increases of course enormously with rising temperature.

A remarkable result of the investigation is the very considerable increase of the dissociation under rising pressure, a phenomenon seemingly explainable only by the lack of strict proportionality between the partial pressures of the gases and their molecular concentrations.

J. E. Trevor.

Cornell University.

Handbuch der Stereochemie. Edited by C. A. Bischoff, Professor of Chemistry at the Polytechnicum of Riga, with the assistance of Paul Walden, Docent in Physical Chemistry. First volume, pp. 448. 8vo. Ill. (M. 14). Frankfurt: Bechhold, 1893.

To those who have not followed with special attention the progress of stereochemistry, it will be a surprise to find Le Bel speaking of this as "a positive science which deserves the place it has gained in our colleges"; to know that for some years a "professor of stereochemistry" has been lecturing at the University of Geneva, and finally to learn that a work so extensive as Prof. Bischoff's could be written about a branch of chemistry of which seven years ago nothing was heard.

As its name implies, this book is intended chiefly for reference. The bulk of the first volume consists of data concerning the optical rotation of all active organic substances; and the great number of constants here collated by Dr. Walden will have permanent value.

The "Historical Introduction" by Prof. Bischoff is full without being tedious. The principal chemists concerned are allowed to speak in their own words; and (except in the case of his own theories) there is no criticism by the author.

It must be observed that the experimental work of Burch and Marsh (called Bush and March) receives no more attention than that accorded to the spelling of their names; and the aromatic-ring theory of Marsh is also overlooked.

On the other hand it is a satisfaction to find that the theories of Van't Hoff and of Le Bel are here recognized as two and distinct. Due importance is accorded to Le Bel's proof of the existence of asymmetric nitrogen, and his attempts to prove the activity of non-saturated carbon compounds "promise a still greater revolution in the prevailing principles of stereochemistry." Unless such a revolution should occur we shall find confronting us this singular situation: the elaboration of the idea of the three-dimensional arrangement of atoms will have shown that in most cases either the arrangements are two-dimensional or there is no permanent arrangement at all. For if a substance $C_3R_1R_2R_3R_4$ (for

example) is inactive, this must be either because the atoms, like those of $C_aR_1R_2R_3R_4$, are in the same plane, or because they incessantly change places. (The tetrahedron hypothesis demands, of course, a three-dimensional arrangement for $C_aR_1R_2R_3R_4$.)

The second volume of Prof. Bischoff's book will be awaited with interest: it will treat of the influence of space-relations on chemical reactions, and of the motion of the atoms within the molecule. ARNOLD EILOART.

A SYSTEM OF INSTRUCTION IN QUALITATIVE CHEMICAL ANALYSIS. By ARTHUR H. ELLIOTT, Ph. D., Professor of Chemistry and Physics, and Director of the Chemical Laboratory in the College of Pharmacy of the City of New York. Second Edition, 1894. Published by the Author.

The first edition of Prof. Elliott's manual has already been favorably criticized in this journal.[1] In the preface to the second edition the author says that it has been adopted as text-book by a number of institutions. The book deserves success and can be recommended for its clearness and attention to details. E. R.

CENTENARY COMMEMORATION OF ANTOINE-LAURENT LAVOISIER, 1794—May 8—1894.

Dr. Gustavus Hinrichs, of St. Louis, has issued a circular letter calling upon chemists to contribute the funds necessary for the erection in the city of Paris of a monument to Lavoisier. The principal part of the letter is here reproduced:

"An entire century has rolled over the unmarked grave of the Copernicus of Chemistry; with to-day, the second century takes its beginning. Will not the chemists of the world deem it a privilege to erect a monument to the memory of their common master who fell a victim to the frenzy of the Reign of Terror? And will not the chemists of France open the way and furnish a place for it to permit us to enjoy that privilege?

"The life-work of Lavoisier was deeper and broader than the discovery of any new substance, and affected the very foundation of the science of chemistry. He broke through the veil of mere phenomena and discovered beyond it the reality of chemical processes.

"History teaches that in every science man has first mistaken the direct testimony of his senses, the mere appearances or phenomena, for the essence of things real, and that only a master-mind can penetrate this veil in which our senses wrap the reality of things and hide it from our reason.

[1] 15, 373.

"The work of Lavoisier is exactly of the same character as that of Copernicus; his system is equally bold, and as plainly contradicted by the immediate testimony of the senses. That is the reason why Scheele and Priestley never surrendered, though they themselves had discovered the very substance which, in the hands of Lavoisier, became the corner-stone of the new system of chemistry. The direct testimony of the senses is undoubtedly that fire-stuff, phlogiston, is set free when carbon, sulphur and the metals do burn. The customary superficial representation of the phlogistic period is as unjust to the eminent chemists of that period as to their opponents.

"Indeed, it required the mind of a Lavoisier, and its persistent labor for twenty years, to accomplish the Copernican revolution in chemistry. He had to devise those admirable experiments with air and metals which demonstrate, once for all, that also in chemistry the testimony of the senses has been misleading, and that where phlogiston appears to be given off, an invisible substance is really taken up. Lavoisier did not tire till he had, balance in hand, demonstrated that in all chemical processes, the sum-total of matter involved remains exactly the same (Traité, I, p. 141), precisely as in the Copernican planetary system the spheres retain their identity and maintain their well-ordered motions unchanged, however much they may appear to wander astray and become retrograde when seen from this earth.

"By the use of his calorimeter, Lavoisier even made a good beginning on the investigation of the dynamic phases of chemical processes.

"Laplace has given (Système du Monde, III. éd., p. 357; 1808) a beautiful word-picture of the life-work of Copernicus; by simply replacing the astronomical terms by their chemical equivalents, this picture changes to a faithful graphic representation of the work of Lavoisier.

"One other fact should be noted to avoid further misconceptions, and especially to forever bar the recurrence of national jealousies. Also on this point the parallel holds good.

"Copernicus is not extolled as a mere observer. Several of his immediate predecessors, as well as many of his followers, greatly surpassed him in this direction. Yet his mind saw clearly many things that the human eye unaided could never have perceived. Not until Galilei, long after the death of Copernicus, had armed himself with his new telescope, did mortal eye behold the moon-like phases of Venus, mentally described by Copernicus; at the same time the telescope revealed a miniature Copernican system in the world of Jupiter.

"In the same manner we will cheerfully grant that some of the contemporaries of Lavoisier may have been more skilled experimenters in some directions, and that no doubt he left much for his followers to do. Nevertheless, his *Traité élémentaire de*

Chimie is unquestionably the first rational exposition of the science of chemistry, entirely resting on experimental evidence, largely his own, and admitting to the list of entities of matter nothing that was not actually produced; and since that day, chemistry is the science of the real elements. This true insight in the nature of matter permitted him to see into the future, as Copernicus had done, and to describe elements before the instrument required to produce them had been invented. When Davy, by means of the powerful galvanic battery of the Royal Institution of Great Britain, produced the light metals, he confirmed what Lavoisier had seen mentally more than thirty years before. (Traité, I, pp. 194, 195.)

"The life-work of Lavoisier has been admirably summed up by Berthelot in the following words (La Révolution Chimique; Paris, 1890; p. 207):

"'That which we have a right to admire, that which the universal judgment of the civilized world with every day hallows more and more, is the positive work which he has accomplished; namely, the final erection, upon a permanent basis, of one of the fundamental sciences, Chemistry. No work in the history of civilization is greater, and therefore the name of Lavoisier will live forever in the memory of humanity.'

"To these clear and true words nothing can possibly be added, except it be the expression of the hope that committees will form in all countries and co-operate with the one that should spring into being at the place of the work and glory, the suffering and death, of Lavoisier. It would be a most encouraging token for the continued progress of our race if the coming twentieth century should find, at the city of Paris, a monument erected to the memory of Lavoisier by the chemists of all the nations of the earth.

"I make bold to suggest the union for this noble purpose by adopting as my own the words spoken in the Collège de France, by Dumas, at the close of his memorial lecture on Lavoisier, on May 7th, 1836:

"'May . . . . this tribute, the feeble expression of the sentiments of veneration which fill my soul . . . . awaken memories and excite the zeal of men in positions of greater influence . . . . that there may be erected, to the memory of Lavoisier, a monument . . . . which to posterity shall express our profound admiration for his genius and our lasting sorrow for his premature death.'"